ELECTRO-OXIDATION OF AMMONIA IN LIQUID PHASE USING GRAPHITE ELECTRODES

BY

TARIQ MOHAMMED

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This thesis, written by **TARIQ MOHAMMED** under the direction of his thesis adviser and approved by his thesis committee, has been presented to and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN CIVIL ENGINEERING**.

Thesis Committee

Dr. Alaadin A. Bukhari (Adviser)

Dr. Ahsan M. Shemsi (Member)

Dr. Muhammad H. Al-Malack (Member)

26 FEB 2015

Dr. Nedal T. Ratrout
Department Chairman

Dr. Salam A. Zummo
Dean of Graduate Studies

4/3/15
Date

This is dedicated to my parents, grandparents, my son Sa'ad and his mother

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All praise and thanks be to Allah (subhaanahu wa ta'aala), the Creator and Sustainer of the Worlds. The completion of this thesis is only one among the innumerable favors He has bestowed upon me, for all of which I hope to be a grateful slave.

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May this be included in our good deeds, and prove to be a beneficial research to the scientific community and mankind as a whole.

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THESIS ABSTRACT

NAME:	Tariq Mohammed
TITLE OF STUDY:	Electro-oxidation of ammonia in Liquid phase using Graphite Electrodes
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This study made use of graphite electrodes for the electro-oxidation treatment of synthetic ammonia solutions in a lab-scale batch reactor. Electro-oxidation offers an alternative to conventional methods for ammonia removal from wastewater. The study determined optimum values of applied current and chloride content, evaluated the effects of initial pH and varying initial ammonia concentration, and monitored the formation of nitrates. It was established that ammonia was removed by the indirect oxidation mechanism involving hypochlorous acid. Current densities from 2.6-15.5 mA/cm^2 were used for samples containing 40-600 mg/L Total Ammonia Nitrogen (TAN) and 600-30,000 mg/L chlorides for a treatment period of 130 minutes. It was found that high chloride content ($\geq$3,000 mg/L) is required for effective ammonia degradation, with removal being enhanced by in-

crease in chloride concentration and applied current. The initial pH does not seem to affect the process significantly. 95% removal was achieved within 90 minutes for samples containing 40 mg/L TAN and 6,061 mg/L chloride at a current of 3.0 A (15.5 mA/cm^2) and voltage of 9.5 V. Energy consumption was also calculated and found to be 3 Ah/L (28.5 kWh/m^3) for these conditions. It was concluded that graphite offers a suitable alternative to other expensive anode materials (such as platinum and titanium) being investigated for ammonia removal from wastewater.

MASTER OF SCIENCE

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Dhahran, Saudi Arabia

ARABIC ABSTRACT

ملخص الرسالة

الإسم: طارق محمد

عنوان الرسالة: الأكسدة الكهربائية للأمونيا في الطور السائل باستخدام أقطاب الجرافيت

التخصص: الهندسة المدنية

تاريخ التخرج: فبراير ٢٠١٥ م

تم في هذه الدراسة استخدام أقطاب الجرافيت للمعالجة بالأكسدة الكهربائية لمحاليل الأمونيا الإصطناعية في المختبر. الأكسدة الكهربائية تقدم بديلا للطرق التقليدية لإزالة الأمونيا من مياه الصرف الصحي. حددت الدراسة القيم المثلى للتيار ومحتوى الكلوريد، وكذلك تقييم آثار درجة الحموضة الأولية وتركيز الأمونيا الأولي المتغير، ورصدت تشكل النترات.

وقد ثبت أنه تمت إزالة الأمونيا من خلال آلية الأكسدة غير المباشرة التي تحتوي على حامض الهيبوكلوروز. وذلك بإستخدام شدة تيار من ٢,٦ حتى ١٥,٥ مللي أمبير/سم^{٢} للعينات التي تحتوي على ٤٠-٦٠٠ ملغ/لتر من أمونيا النيتروجين الكلي (TAN) و٦٠٠-٣٠٠٠٠ ملغ/لتر من تركيز الكلوريد لفترة معالجة بلغت ١٣٠ دقيقة. وقد وجد أن نسبة عالية من الكلوريد (≤ ٣٠٠٠ ملغ/لتر) مطلوبة لإزالة الأمونيا بفعالية، وترتفع درجة الإزالة مع زيادة تركيز الكلوريد وشدة التيار المار.وجد أن درجة الحموضة الأولية ليس لها تأثير كبير على العملية. وقد تحقق إزالة ٩٥٪ من TAN في غضون ٩٠ دقيقة للعينات التي تحتوي على ٤٠ ملغ/لتر TAN و٦٠٦١ ملغ/لتر كلوريد لتيار يبلغ ٣,٠ أمبير (١٥,٥ مللي أمبير/سم^{٢}) وجهد ٩,٥ فولت. تم أيضا حساب إستهلاك الطاقة ووجد أنها ٣ أمبير ساعة/لتر (٢٨,٥ كيلو واط ساعة/م^{٣}) لهذه الظروف التجريبية. وخلص إلى أن الجرافيت يقدم بديلا مناسبا لغيره من مواد الأنود مرتفعة التكلفة (مثل البلاتين والتيتانيوم) المستخدم في تجارب إزالة الأمونيا من مياه الصرف الصحي.

درجة الماجستير

جامعة الملك فهد للبترول والمعادن

الظهران – المملكة العربية السعودية

فبراير ٢٠١٥ م

CHAPTER 1

INTRODUCTION

Ammonia (NH_3) is a chemical compound formed by one atom of nitrogen with three atoms of hydrogen. It is a colorless gas with a pungent smell, and a pollutant in both gaseous and aqueous form. Aqueous ammonia is a hazard to human health at high concentrations ($> 20\%$) owing to its corrosive nature, thereby affecting the eyes and skin [1]. Ingestion can cause damage to the mucous membranes of the oesophagus and stomach [2]. However the threat posed to the environment is more serious since it is toxic to fish and other aquatic organisms at much lower concentrations (even at 1.86 mg/L) [3]. Eutrophication is another major threat posed to the environment by aqueous ammonia, wherein the dissolved oxygen (DO) in the water is depleted due to proliferation of undesirable plant species thereby affecting aquatic organisms. Gaseous ammonia has a strong pungent smell that can be perceived by most people at concentration of 35 mg/m^3, is an irritant to the eyes and respiratory tract at more than 50 mg/m^3 and can cause severe respiratory distress at 1000 mg/m^3 [2].

Ammonia is one of the important parameters that need to be considered in wastewater treatment, other parameters being turbidity, pH, temperature, Total Suspended Solids (TSS), Total Dissolved Solids (TDS), alkalinity, Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), chloride (Cl^-), Total Kjeldahl Nitrogen (TKN), phosphorus etc. Wastewater can be broadly classified as domestic and industrial. Domestic or municipal wastewater is collected from the residential buildings, institutions, hospitals and commercial complexes in a locality by means of sewage networks and carried to a common wastewater treatment plant (WWTP) or sewage treatment plant (STP) either by gravity or by pumping from different pumping stations located strategically. In areas where there is no sewage network, trucks may be used to collect sewage from septic tanks and transport it to the treatment facility.

Industrial wastewater refers to the liquid wastes that are discharged from industries and since there are many different industries with diverse operations, the effluents are also vary chemically. It is therefore practically impossible to arrive at typical values for pollutants in an industrial effluent. However pulp and paper mills, gas and coke plants, aquaculture and animal-rearing farms are known to produce effluents high in ammonia. Coking effluents with up to 2,500 mg NH_3/L have been reported by Ozyonar(2012) [4].

1.1 Sources of Ammonia in Wastewater

The major source of ammonia in municipal wastewaters is human waste, while the presence of ammonia is also high in effluents from certain industries such as pulp and paper mills, fertilizers, coking facilities and gas plants. Large animal-rearing facilities such as aquaculture units and poultry farms also produce a significant quantity of ammonia. It is also present in household cleaners and window-cleaning solutions, from which it may possibly be discharged to the wastewater stream.

Ammonia levels in rivers and lakes may exceed safe exposure limits due to improper treatment of municipal or industrial effluents, decomposition of biological wastes, agricultural run-off and deposition from atmosphere. Around 80% of all ammonia manufactured is used as fertilizers [5], so the run-off from the areas where these fertilizers are applied may contain high levels of ammonia. Industrial emissions of ammonia into the atmosphere could also be deposited into the aquatic environment by precipitation [3, 6].

1.2 Ammonia Hazards

Ammonia in its aqueous form is not considered to be a serious hazard to human health [7] except in the case of very high concentrations ($> 20\%$) [1] when it is corrosive to the skin and eyes and can even cause permanent blindness. Damage can also be caused to the mucous membranes of the food-pipe and stomach [2]. It is not known to be carcinogenic [1]. The human body has a mechanism to detoxify ammonia, therefore it has a toxic effect only if this detoxification capacity

is exceeded [7]. Such exposure occurs rarely, except in the case of contact with household cleaners or solution with high ammonia concentration. However, fish and other aquatic organisms do not have this capability for detoxification, thus rendering them very susceptible to ammonia toxicity at very low concentrations. The average mean acute toxicity value for 32 species of freshwater fish is 2.79 mg NH_3/L, while it is 1.86 mg NH_3/L for 17 species of marine fish [3].

Eutrophication is another major concern related to ammonia. Ammonia contains nitrogen, which is a macro-nutrient for plant growth. Therefore, when any water body contains a high concentration of ammonia, it promotes the growth of unwanted organisms such as algae and other phytoplankton. Dissolved oxygen (DO) in the water is then depleted because these undesirable organisms compete with other aquatic organisms for the available oxygen. This leads to fish fatality and loss of coral reef communities [8]. In addition the transparency of the water is also affected and changes may be observed in the taste, odor and color [9]. Eutrophication is acknowledged as a major threat to water bodies worldwide which include lakes, streams, rivers, and even seas, as in the case of the Baltic, Black and Adriatic seas in Europe [10]. Extensive studies are being carried out to understand the factors governing this phenomenon, and the possible steps to control it. However, it is clear that among other nutrients such as phosphorus and silicon, the concentrations of nitrogen, and therefore ammonia in effluents, play a significant role [8, 11, 12].

Ammonia also contributes towards soil acidification when it reacts with water

to form ammonium ion (NH_4^+) and permeates into the soil. This may further dissociate or undergo nitrification to nitrite (NO_2^-) or nitrate (NO_3^-) by the action of nitrifying bacteria. This is accompanied by the release of H^+ ions into the soil, thus leading to acidification of the soil [13].

There are numerous reported instances of ammonia spills leading to fish fatality. In August 2008, two huge fish mortalities of 3.9 million and 750,000 were reported in the Pamlico and Neuse rivers respectively in the US state of North Carolina. Both rivers had high nutrient levels, leading to algal blooms and as a result killing large numbers of fish [14]. More than 100,000 fish were killed when effluent with high ammonia concentration was released into the sewerage while boilers were being cleaned at the University of Illinois Abbott power plant in July 2002 [15]. In December 2001, about 1.3 million fish were killed in the Des Moines River, Iowa, USA following an ammonia leak from a pipeline [16]. 100 tonnes of tilapia fish were reportedly killed in Lake Buhi, Philippines in November 2010. The water was found to have very low dissolved oxygen and very high ammonia concentration [17].

1.3 Regulatory limits for ammonia

It is noteworthy that there are different parameters such as TAN, TKN and TN which are used to quantify the ammonia and nitrogen content in wastewater. Total Ammonia Nitrogen (TAN) is the term used to refer to the sum of ammonia (NH_3) and ammonium (NH_4^+), while Total Kjeldahl Nitrogen (TKN) is the sum of organic

nitrogen, ammonia (NH_3) and ammonium (NH_4^+). Total Nitrogen (TN) is the sum of organic nitrogen, nitrite (NO_2^-), nitrate (NO_3^-) and TAN, all expressed in terms of nitrogen. Unionized ammonia (NH_3) is more dangerous than its ionized form (NH_4^+) because most biological membranes are permeable to ammonia (NH_3), but not to the ammonium ions (NH_4^+) [3].

The permissible ammonia levels in wastewater vary significantly based on country, effluent source and the type of water body into which discharge takes place. Toxicity values for fish are the major criteria used to determine these regulatory limits. The US EPA ammonia limits amended in 2013 are based on the sensitivity of freshwater mussels and snails [18]. The toxicity values depend significantly on the water pH, since ammonia exists in its unionized form in alkaline conditions, which is more toxic to marine life. From Fig.1.1, it can be seen that although temperature has an effect, pH is the major factor that determines the distribution of unionized ammonia and ammonium ions.

With regard to the legal limits for pollutants, it is noteworthy that developed countries have more stringent environmental regulations as compared to underdeveloped countries. US EPA recommends a chronic concentration range of 0.99-4.4 mg TAN/L, and an acute value range of 7.3-38.9 mg TAN/L for temperatures 30^0 C - 0^0 C respectively at neutral pH. The acute value is the one-hour average that should not be exceeded more than once every three years. Furthermore, 2.5 times of the chronic value should not be exceeded by the highest four-day average within a 30-day period more than once in three years [18].

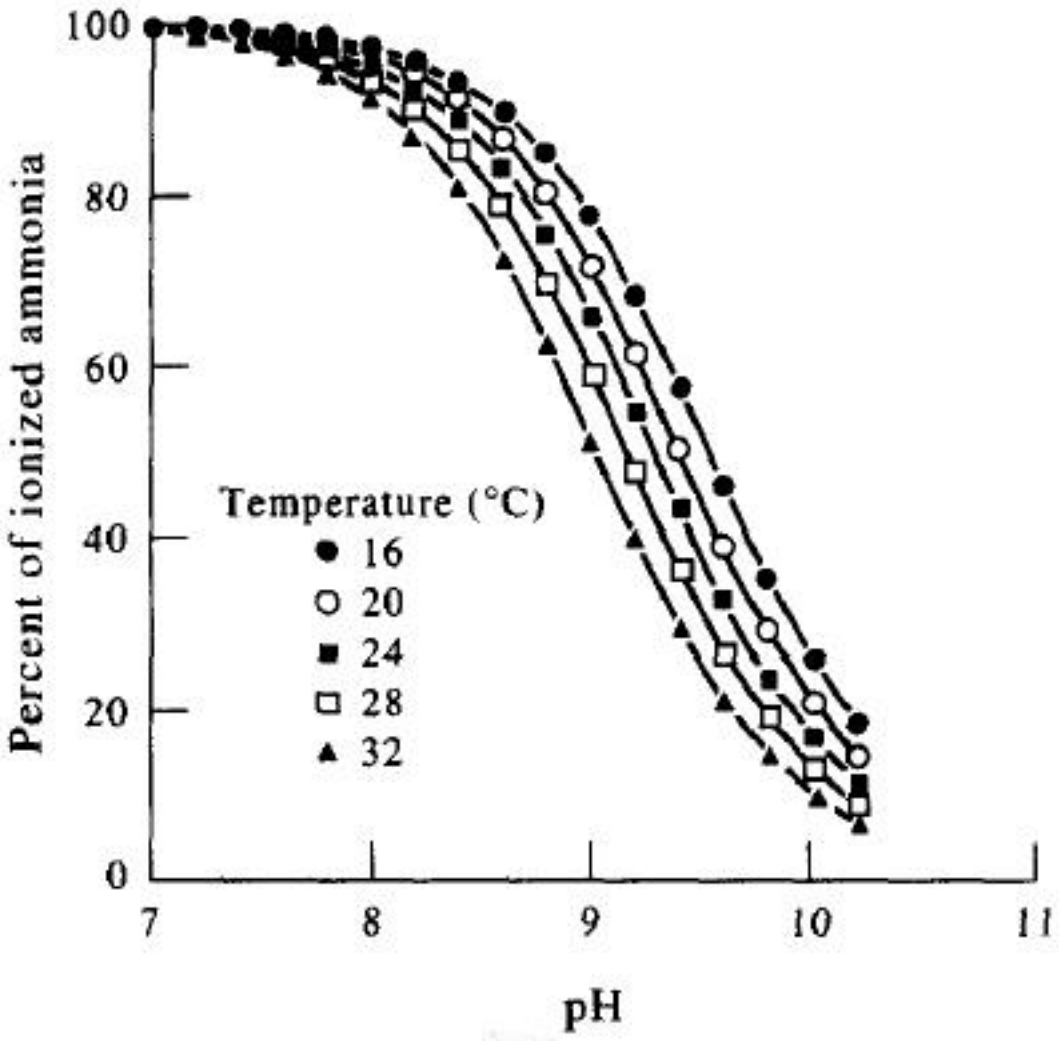


Figure 1.1: Percent of un-ionized ammonia (NH_3) existing in the aqueous solution as a function of pH at various temperatures

[Source: Lin and Wu (1996) [19]]

In Saudi Arabia, the maximum permissible limit of TAN is 1 mg/L for discharge into marine and eco-sensitive areas while industrial effluents are allowed up to 3 mg/L [20]. Chinese regulations allow a maximum concentration of 25 mg TAN/L [21]. Indian standards specify the maximum allowable limits of TAN, TKN and free ammonia (NH_3) as 50, 100 and 5 mg/L respectively for discharge into any water body [22]. The European Union stipulates maximum total ammonia of 1.1 mg/L for discharges into rivers upland and having low alkalinity, whereas rivers lying lowland and highly alkaline have a limit of 2.5 mg/L [23]. Malaysia has limits of 5 mg/L and 10 mg/L for ammoniacal nitrogen and nitrate respectively [24].

South Korean regulations permit 40 mg/L of total nitrogen for effluent from wastewater treatments plants with capacity less than 50 m^3/day and 20 mg/L for treatment plants with greater capacity. During winter, the discharge limits are raised to 60 mg/L regardless of plant capacity [25]. In Germany, the ammoniacal nitrogen should not exceed 10 mg/L at the point of discharge for domestic wastewater, while other parameters such as total nitrogen and nitrate also have standards defined for various industrial effluents [26]. Japan meanwhile has a relatively high effluent limit of 120 mg/L with a daily average limit of 60 mg/L [27].

1.4 Significance of present study

Many different technologies have been used to treat wastewater. The conventional processes such as physico-chemical (air-stripping, ion-exchange, break-point chlo-

rination, reverse osmosis) and biological methods (activated sludge, extended aeration, sequencing batch reactors, fixed film bio-reactors) have been extensively explored and they have been in practice for many decades. However, electrochemical methods, which are relatively new compared to the conventional physical, chemical and biological treatment processes, are being investigated for their efficiency and feasibility. The use of electricity for treating water was first proposed in the UK in 1889 [28]. Processes such as electro-coagulation, electro-deposition, electroflotation and electro-oxidation in treating wastewaters from various sources are well-established [28].

Electro-oxidation involves oxidation of target pollutants at the anode of an electrochemical cell. This process is used to decompose the target contaminant using suitable electrodes in an electrolytic cell. Application of voltage causes electrolysis with concomitant decomposition of contaminant. Important factors that affect the efficiency of the process include electrode materials, applied current, electrolyte concentration, pH and the presence of mediators [28].

The present research aims to investigate the performance of graphite electrodes in the removal of ammonia from solution. Many different electrode materials (platinum, titanium, iridium, boron-doped diamond, rhodium etc.) have been studied over the years, as mentioned in Ch.2. However there was found to be lack of adequate research using graphite for the electro-oxidation of ammonia. Therefore, this study was conducted in order to explore the applicability of graphite electrodes for this purpose and be a reference in the literature related to

this particular field. The main objectives of this study include establishing the optimum operational parameters for ammonia removal, ie., applied current and sodium chloride concentration. In addition, the effects of initial pH and varying initial concentrations of ammonia were also investigated, along with the power consumption of the process.

CHAPTER 2

LITERATURE REVIEW

2.1 Current Practices of Ammonia Removal and their limitations

The conventional methods of ammonia removal include break-point chlorination, air stripping, ion-exchange membranes and biological processes. Each method has advantages and disadvantages, which are discussed in the following paragraphs.

Several different biological treatment methods are employed for ammonia removal. All these methods are based on two steps - nitrification and denitrification. Nitrification, or conversion of ammonia to nitrite (NO_2^-) and then to nitrate (NO_3^-), is achieved with the help of autotrophic bacteria, which require O_2 as oxidizing agent and CO_2 or HCO_3^- as carbon source for oxidizing ammonia. Denitrification is also a two-step process in which the nitrate is initially converted to nitrite, which is then converted to nitrogen gas. The bacteria involved here require organic carbon as opposed to oxygen in the nitrification stage. Carbon is usually

supplied before the denitrification filter as methanol, ethanol or sugar in liquid form. Biological methods in general (nitrification and denitrification stages) require large systems and longer retention periods as compared to physico-chemical methods [29].

Conventional activated sludge treatment, one of the commonly used biological methods, consists of an aeration basin followed by a secondary clarifier. The ammonia removal takes place in the aeration tank, while the Return Activated Sludge (RAS) and Waste Activated Sludge (WAS) are collected in the secondary clarifier. This system is relatively easy to operate and can handle different types of wastewater. The disadvantages, however, include high capital costs associated with the large aeration tanks, high costs of mechanical equipment such as blowers, pumps, clarifier mechanisms etc. Sludge-bulking due to filamentous organisms is also an issue. [24, 30–33]

Extended aeration is another biological method very similar to the Activated Sludge treatment, the main difference being that longer Hydraulic Residence Times (HRT) and Solids Residence Times (SRT) are required. HRT is typically 24 hours, whereas SRT can be over 20 days. These systems give effluents with higher quality and are even easier to operate than conventional activated sludge systems. However, larger aeration tank is necessary thereby making this feasible only for smaller volumes of wastewater. [30, 34, 35]

Sequencing Batch Reactors (SBR) use the same process as activated sludge, but the same tank is used for aeration and clarification. Each sequence consists

of four steps - fill, react/aeration, settle, decant. The facilities required by this method are compact in size and eliminates the need for RAS or separate clarification equipment. However, there is the obvious drawback that comes with any batch reactor, that it remains out of operation during the settling and decanting stages. This necessitates having several tanks to manage the flow of wastewater. [30, 36, 37]

Fixed film bio-reactors are those in which the micro-organisms are attached to fixed media as opposed to activated sludge processes where they are in suspension. Trickling filters, Rotating Biological Contactors (RBC) and Moving Bed Bio-Reactors (MBBR) are some of the types of fixed film. These have relatively high SRT and pumping energy requirements, while sloughing is an added limitation. MBBRs require high levels of dissolved oxygen (up to 7 mg/L). [38–42]

In the case of Membrane Bio-Reactors (MBR), raw wastewater is first finely screened before it enters an anoxic basin, from where mixed liquor flows into pre-aerated basins and subsequently enters the MBRs. The effluent from this treatment has high quality and there is no need for additional clarification or filtration. Moreover, the area requirements are relatively smaller. However, construction is expensive and there are costs associated with replacement of membranes. This method also requires more power and operator attention. [30, 43]

Air stripping, which is a commonly used method to treat wastewater containing ammonia, involves the removal of ammonia from liquid stream into air that is passed upwards through a stripping tower. It only removes ammonia from one

phase (liquid) and puts in back into another (air). Moreover, this process requires a high pH (10.8-11.5) and this would imply the addition of chemicals such as lime to raise the pH. It also necessitates construction of stripping towers, pumping of wastewater and air into these stripping towers, and ultimately the air stream may also require treatment. In addition, this method is also not economically feasible for ammonia concentrations greater than 100 mg/L. [44–46]

Reverse Osmosis (RO) treatment is another method that delivers very high quality water. It also gives high permeability for selective ions. However, the operating costs are high and the ammonia removed from the wastewater is accumulated in the brine system, which requires further treatment. Moreover the fouling of membranes is another limitation that affects performance of this treatment. [47–49]

Ion-exchange methods of ammonia removal have also attracted much attention. This process typically involves passing the ammonia-contaminated water through a column filled with zeolite or other materials which have affinity towards ammonia. Ammonia is adsorbed by the resins inside the column and treated water leaves the column. This is a quick method with relatively less initial investment. However the costs associated with regeneration lead to increased operation costs. There is also a chance of desorption in the case of low-ammonia influent, due to shift in exchange equilibrium. Activated carbon method is very similar in principle, however the material used is activated carbon which is an adsorbent with several desirable properties such as large surface area, controllable pore structure,

high thermal stability and low acid-base reactivity. This is also an expensive material and regeneration is expensive as well. [50–53]

Break-point chlorination is another conventional method used to remove ammonia from water. This method depends on the generation of hypochlorous acid by the reaction of water with chlorine in the form of chlorine gas, calcium hypochlorite or sodium hypochlorite. Each of these ways for generating hypochlorous acid has its limitations. Chlorine gas is the most efficient and effective, but it is toxic, heavy, corrosive and an irritant to the respiratory system, skin and eyes, thereby posing great risk in handling. It can be fatal even at a concentration of 1000 ppm, and is usually compressed into liquid form and stored in metal cylinders. Calcium hypochlorite, usually available as tablets or in granular form, is very corrosive and requires careful handling. It is not easily dissolved, and the chlorine concentration achieved in solution depends on the extent of dissolution. If kept near organic materials such as cloth, petrol or wood, the combination can produce enough heat for an explosion. Exposure to moisture can lead to the formation of chlorine gas, which is toxic. Sodium hypochlorite, though the easiest of the three to handle, is also extremely corrosive and requires storage in a cool, dark and dry place. Moreover, it decomposes naturally, which prevents storage periods of more than a month [54, 55]

Having briefly studied the technologies presently in use for ammonia removal from wastewater, their respective advantages and disadvantages, it is now required to explore the significance of electro-oxidation as an option for ammonia removal.

It needs to be determined whether the limitations of the current practices can be overcome by electro-oxidation.

2.2 Electro-oxidation

2.2.1 Introduction

Electro-chemical treatment has been extensively applied to effluents from municipal sewer networks, tanneries, electro-plating, dairy, textile processing and numerous other industries with successful results [28]. Electro-flotation, electro-coagulation, electro-deposition and electro-dialysis are some of the commonly used methods besides electro-oxidation that make use of electricity for wastewater treatment [28].

The electro-oxidation process involves two (or more) electrodes dipped into the electrolyte contained in a vessel. An external power is supplied to the electrodes (positively charged anode and negatively charged cathode). The anions migrate towards the anode and get oxidized by losing electrons, while the cations move towards the cathode where they gain electrons, thereby getting reduced. Thus the decomposition of target pollutants is achieved on the anode of the electrolytic cell in the case of the target pollutants being anions, and the treatment is said to take place by electro-oxidation. On the other hand, in the case of pollutants being cations, the treatment method is called electro-reduction and the decomposition of pollutants is achieved at cathode.

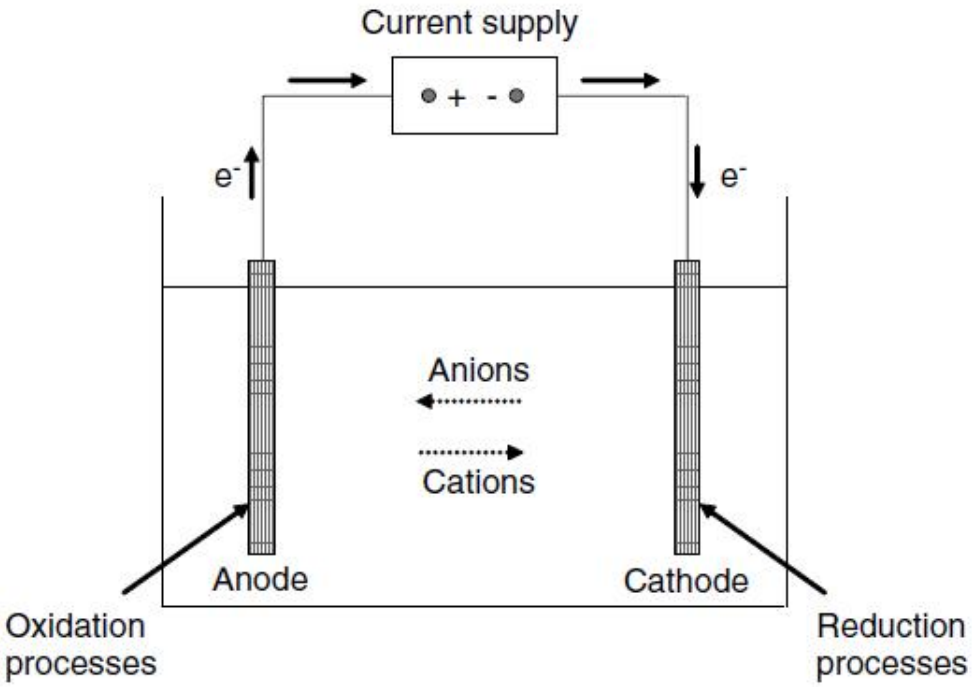


Figure 2.1: Conceptual diagram of an Electro-chemical reactor

[Source: Anglada et al.(2009) [56]]

The conceptual diagram of the electro-chemical treatment process is shown in Fig.2.1. The selection of anode material, applied current, electrolyte concentration and initial pH are some of the factors that affect the process efficiency [57].

2.2.2 Mechanism

Electro-oxidation can be classified as direct or indirect based on the mechanism involved. In the case of direct electro-oxidation, also known as anodic oxidation, the decomposition of pollutants is achieved at the anode by the generation of hydroxide ions [58] or active oxygen that may be adsorbed physically ($^{\bullet}OH$) or chemically ($MO_x + 1$) [28]. In the case of indirect electro-oxidation, oxidants such as chlorine and hypochlorite generated at the anodes causes the decomposition of target pollutants [28].

Electro-oxidation by the direct mechanism involves the migration of pollutants to the anode, where they are oxidized. This is depicted in Fig.2.2. This is also known as anodic oxidation. In the case of ammonia, anodic oxidation takes place due to hydroxide ions [58].

Suggested direct mechanism:

At cathode:

$$6H_2O + 6e^- \rightarrow 3H_2(g) + 6OH^- \tag{2.1}$$

In bulk solution:

$$2NH_3(aq) + 6OH^- \rightarrow N_2(g) + 6H_2O + 6e^- \tag{2.2}$$

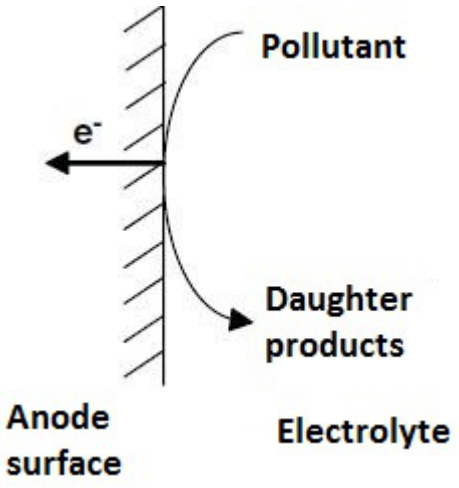


Figure 2.2: Direct Oxidation

[Adapted from Anglada et al.(2009) [56]

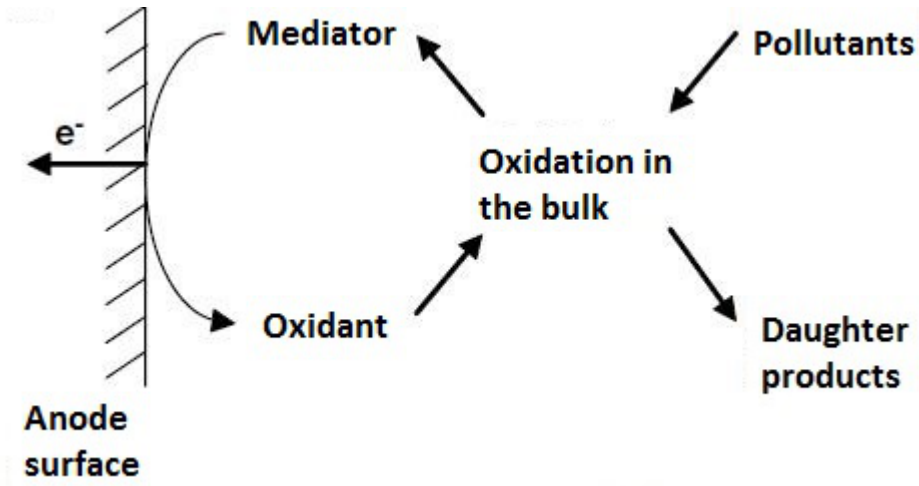


Figure 2.3: Indirect Oxidation

[Adapted from Anglada et al.(2009) [56]

Overall reaction:

$$2NH_3(aq) \rightarrow N_2(g) + 3H_2(g) \tag{2.3}$$

[Source: Boggs and Botte (2010) [58]]

For indirect electro-oxidation, ammonia is oxidized not directly at the anode, but by anodically generated oxidizing agents such as chlorine, hypochlorous acid, hydrogen peroxide, ozone and mediators such as Ag^{2+}, Co^{3+}, Fe^{3+}, Ce^{4+} [28]. Of these, hypochlorous acid is regarded to be the most effective [55]. The generated oxidants react with ammonia in the bulk solution as opposed to the anode surface in the case of direct electro-oxidation. The reactions involved are shown in equations 2.4-2.8 and as given in Fig.2.3 and Fig.2.4. Mediated electro-oxidation involves the oxidation of metal ions called mediators on the anode from a stable low valence state to a reactive high valence state which enables it to degrade pollutants. However this process requires highly acidic environment and has the additional drawback of contamination with heavy metals.

Suggested indirect mechanism

At anode:

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{2.4}$$

In solution:

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \tag{2.5}$$

$$HOCl + (2/3)NH_3 \rightarrow (1/3)N_2 + H_2O + H^+ + Cl^- \tag{2.6}$$

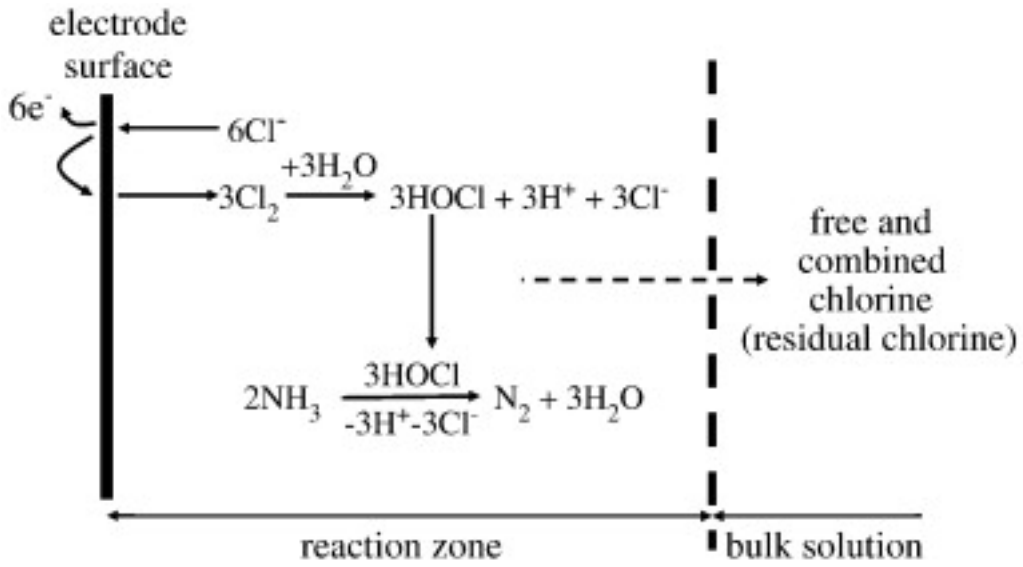


Figure 2.4: Electrogenerated active chlorine/ammonia reaction close to the anode surface

[Source: Kapalka et al.(2010) [59]

$$HOCl + (2/3)NH_4^+ \rightarrow (1/3)N_2 + H_2O + (5/3)H^+ + Cl^- \quad (2.7)$$

$$HOCl + (1/4)NH_4^+ \rightarrow (1/4)NO_3^- + (1/4)H_2O + (3/2)H^+ + Cl^- \quad (2.8)$$

[Source: Liu et al.(2009) [60]

2.3 Previous work on ammonia removal

The studies by Katan and Galiotto (1963), Oswin and Solomon (1963), Sparbier and Wolf (1964), Despic et al. (1966) [61], Gerischer and Mauerer (1970) [62], Sasaki and Hisatomi (1970) and Marincic and Leitz (1977) were the earliest documented research on the use of electro-oxidation for ammonia removal [63, 64]. It was established by these studies that platinum black anodes and platinized platinum can oxidize ammonia to nitrogen.

The selection of anode material is one of the most important factors affecting the process efficiency. As stated previously, platinum was the first successful anode material for ammonia electro-oxidation. Although ammonia removal was good, economic considerations made it unviable as a commercial option. The focus then shifted towards the use of anodes which had platinum deposition rather than pure platinum. There were favorable results using these platinum-loaded anodes, but this too was not an economically feasible option [28]. Research is still being

conducted using other noble metals such as iridium (Ir) [59,60,65–67], ruthenium (Ru) [65,68–71], rhodium (Rh) [67], palladium (Pd) [67] and their oxides, as well as titanium (Ti) [59,60,66–72].

The major objective of these explorations regarding anode materials is to find a material that has high electrical conductivity, resistance to erosion and corrosion and low cost/life ratio, in addition to efficient oxidation of target pollutant(ammonia) [56]. The oxygen evolution potential is a major factor that determines the efficiency of an anode. This term is used to refer to the potential required for the oxygen evolution reaction (equation 2.9) to take place. The values for different anodes are listed in Table 2.1, reported by Chen (2004) [28].

$$2H_2O - 4e^- \rightarrow O_2 + 4H^+ \tag{2.9}$$

When the applied potential is higher than the value of oxygen evolution potential for a particular anode, there is wastage of current because the reaction consumes a significant amount of current. This negatively affects the formation of oxidizing agents such as hypochlorous acid or chlorine. It is therefore advantageous to use anodes with high oxygen over-potentials. The formation potentials of different oxidizing agents are listed in Table 2.2.

Table 2.1: Potential of Oxygen evolution of different anodes, Volts vs. NHE

Anode	**Voltage (V)**	**Conditions**
Pt	1.3	0.5 M H_2SO_4
Pt	1.6	0.5 M H_2SO_4
IrO_2	1.6	0.5 M H_2SO_4
Graphite	1.7	0.5 M H_2SO_4
PbO_2	1.9	1.0 M $HClO_4$
SnO_2	1.9	0.5 M H_2SO_4
PbSn (93:7)	2.5	0.5 M H_2SO_4
Ebonex (titanium oxides)	2.2	1 M H_2SO_4
Si/BDD	2.3	0.5 M H_2SO_4
Ti/BDD	2.7	0.5 M H_2SO_4
DiaChem	2.8	0.5 M H_2SO_4

[Source: Chen (2004) [28]]

Table 2.2: Formation Potential of typical chemical reactants

Oxidants	**Formation potential (V)**
$H_2O/^{\bullet}OH$ (hydroxyl radical)	2.80
O_2/O_3 (ozone)	2.07
$SO_4^{2-}/S_2O_8^{2-}$ (peroxodisulfate)	2.01
MnO_2/MnO_4^{2-} (permanganate ion)	1.77
H_2O/H_2O_2 (hydrogen peroxide)	1.77
Cl^-/ClO_2^- (chlorine dioxide)	1.57
Ag^+/Ag_2^+ (silver(II) ion)	1.5
Cl^-/Cl_2 (chlorine)	1.36
$Cr_3^+/Cr_2O_7^{2-}$ (dichromate)	1.23
H_2O/O_2 (oxygen)	1.23

[Source: Chen (2004) [28]]

Vlyssides et al. (2002) [72], used Ti/Pt anode in a pilot plant with 15 L capacity. Cylindrical Ti electrodes 48 cm in length and 2.54 cm in diameter were used along with stainless steel cathode. pH was controlled by means of adding HCl and NaOH. It was observed that alkaline conditions favored ammonia removal. The fastest ammonia removal was achieved at pH 9, followed by 6, 8 and 7 respectively. 82% reduction in ammonia was achieved after a treatment of 1 h at 75 mA/cm^2. The initial ammonia and NaCl concentrations were 150 mg/L and 8,000 mg/L respectively. COD, VSS and phosphorus were the other pollutants removed.

Feng et al. (2003) [69] explored the applicability of Ti/Pt electrodes coated with Ti/RuO_2-TiO_2 for the electro-oxidation of ammonia. A pilot plant with a flow of 0.3 m^3/h was set up and the process invloved both electro-coagulation and electro-oxidation. It was found that from untreated hog-raising wastewater, only 19.5% TAN removal was achieved while 55.6% removal was achieved from the same water when it was pre-treated biologically. At the same current density of 3 mA/cm^2, 81% ammonia removal was achieved from domestic wastewater. The improvement in removal efficiency was attributed to the reduction is suspended solids. Direct electro-oxidation was the mechanism involved in this study. The role of hydroxyl radicals was confirmed by cyclic voltammetric studies.

Vanlangendonck et al. (2005) [70] used Ti covered with Ti/RuO_2 electrodes to treat power plant wastewater with chloride content 2000-12000 mg/L. The effects of current density, pH and other oxygen-containing anions (SO_4^{2-}, CO_3^{2-}

and PO_4^{3-}) were investigated. High chloride content, high current density and absence of co-anions was found to be the optimal condition for ammonia removal. Chloride content was found to have an exponential effect on ammonia removal. At chloride content of 7 g/L, the ammonia oxidation rate achieved was 85 g/h/m^2. However, at chloride concentration 12 g/L, the ammonia oxidation rate was seen to increase only by 10 g/h/m^2. It was also observed that the ammonia removal rate increased from 85 to 200 g/h/m^2 when the current density was increased from 50 to 120 mA/cm^2.

Szpyrkowicz et al. (2005) [67] investigated four different electrode materials - Ti/RhO_x-TiO_2, Ti/PdO-Co_3O_4, Ti/PbO_2 and Ti/Pt-Ir for the treatment of tannery wastewater. The current densities studied were 20 and 40 mA/cm^2, with removal efficiency improving with increase in current density. The chloride content of the samples studied was around 5,000 mg/L. TAN, TKN, COD, sulfides and Cr ions were monitored. It was found that Ti/Pt-Ir and Ti/PdO-Co_3O_4 electrodes performed better than the other two. Electro-oxidation treatment was recommended as a post-treatment for biological processes to remove ammonia at low energy consumption (0.4 kWh/m^3)

Kim et al. (2006) [65] used ruthenium dioxide (RuO_2), iridium dioxide (IrO_2) and platinum anodes to study samples with chloride content up to 10,000 mg/L. The cell used was a very small one (20 ml) with electrode dimensions 2 cm x 4 cm x 0.2 cm. The effects of pH, chloride, anode, current density and initial ammonia concentration were studied. It was found that RuO_2 and IrO_2 electrodes

performed better than Pt in both acidic and alkaline conditions. Maximum removal was observed at 80 mA/cm^2 above which it was suggested that hydroxyl ions interfered with ammonia adsorption at the electrode surface. It was also observed that though higher chloride content showed better removal, the influence of chloride was not significant beyond chloride concentrations of 10 g/L. It is noteworthy, however, that their study showed effective ammonia removal only at a high pH value of 12.

Li and Liu (2009) [68] used RuO_2/Ti anode and steel cathode in a 1 L electrolysis cell to treat synthetic wastewater containing 10-103 mg/L ammonia. The effects of current density, chloride, initial ammonia concentration and pH on ammonia removal were studied. Initial ammonia concentration did not affect the oxidation rate, while the rate of oxidation was enhanced by increase in chloride content and current density. Chloride concentration 30-300 mg/L were studied at current densities 3.8-15.4 mA/cm^2. The highest oxidation rate achieved was 12.3 mg N/L/h. pH 3 showed significantly slower removal while pH 7 showed slightly better removal than pH 9. pH was controlled throughout the experiment. Ammonia removal was attributed to the indirect mechanism.

Liu et al. (2009) [60] also used Ti/IrO_2 in a similar study where the parameters investigated were current density, chloride content, time and pH. The initial ammonia concentration used was 32 mg/L and current densities explored were 3.8-15.4 mA/cm^2. Complete removal was achieved after 3 h at a current density of 15.4 mA/cm^2 and 300 mg/L chloride at a rate of 8.5 mg N/L/h. Increase in

chloride content and current density improved removal efficiency, though the effect of pH was not significant. As opposed to their previous study, it was observed that pH 3 showed quickest removal, followed by pH 7 and then 9.

Kapalka et al. (2010) [73] used Boron-Doped Diamond (BDD) anode to study ammonia removal from synthetic wastewater. A 0.13 L reactor was used with BDD anodes of surface area 12.5 cm^2 and two zirconium cathodes. The specific charge required for complete ammonia removal from an initial concentration of 50 mg/L at pH 5.5 and current density 30 mA/cm^2 was 7 Ah/L. It was inferred that at high pH (>8), the direct electro-oxidation mechanism takes place, whereas below pH 8, the indirect mechanism is responsible for ammonia removal.

Kapalka et al. (2010) [59] also employed Ti/PtO_x-IrO_2 anodes for ammonia removal, using a 0.12 L reactor. The initial TAN of the sample was 950 mg/L and it was completely removed after treatment of 8 Ah/L at current density 20 mA/cm^2 and pH 6. After cyclic voltammetric studies, the indirect oxidation by active chlorine was suggested as the mechanism behind ammonia removal in this case.

Kapalka et al. (2010) [74] then used Ni/$Ni(OH)_2$ anodes with surface area 16.47 cm^2, two zirconium cathodes and a 0.15 L reactor. It was found that the removal was effective only above pH 7, and it was concluded that the mechanism involved was direct electro-oxidation. At pH 11 and 20 mA/cm^2, it took nearly 11 hours to remove 50% TAN from a sample containing 600 mg/L initial TAN. 11% of TAN was converted to nitrate and corrosion of the electrode was observed,

concomitantly releasing Ni to the wastewater.

Ding and Feng (2010) [71] made use of Ti-RuO_2–Pt anode and Ti cathode both with dimensions 11 cm x 4 cm x 0.2 cm to treat ammonia from synthetic wastewater in a 1 L tank. The initial ammonia concentration of the samples was 50 mg/L and sodium chloride content was 0-500 mg/L. Current densities studied were 5-15 mA/cm^2. Current density of 10 mA/cm^2 and sodium chloride concentration 300 mg/L was found to be optimal. At these conditions, ammonia concentration of 4.6 mg/L was achieved after an hour of treatment.

Diaz et al. (2011) [75] used BDD anodes to investigate the influence of current density on ammonia removal from a saline aquaculture effluent. The effluent was doped with ammonium chloride to get an initial ammonia concentration of 8 mg/L for laboratory tests. A 2 L batch reactor was used and the electrodes were BDD (Boron-Doped Diamond) on silicon substrate with an electrode spacing of 1 mm. Current densities from 5-50 mA/cm^2 were used and it was found that at 10 mA/cm^2, 70 minutes were required for 50% ammonia removal. But when the current density was increased to 30 mA/cm^2, the same removal was achieved within 40 minutes and only 20 minutes were required at 50 mA/cm^2.

Yunqing et al. (2011) [66] made use of Ti/IrO_2-SnO_2-Sb_2O_5 anode with Ti cathode in a 0.6 L reactor with electrode surface area 50 cm^2. Current densities 1-5 mA/cm^2 were investigated. 90% removal was achieved within 10 minutes, however the sample had very low initial TAN (2.83 mg/L) and very high chloride content (26,000 mg/L). 2.5 mA/cm^2 was determined to be the optimum current

density and the energy consumption was calculated as 1.75 kWh/m^3.

Zorpas (2011) [76] studied the use of Ti/Pt as anode along with steel cathode for the treatment of domestic wastewater. A pilot scale setup was used with an active area of 3 L fed by a recirculating tank of 50 L. Sodium chloride concentration was 20,000 mg/L and current applied was 105 A. pH was controlled throughout the experiment and it was observed that pH 6 and 8 showed similar removal characteristics while pH 7 was significantly slower.

A summary of reviewed literature is given in Table 2.3.

2.3.1 Graphite electrodes

Graphite is an allotrope of carbon with good electrical conductivity. The use of graphite as an anode material for the electro-oxidation of ammonia is of particular interest primarily on account of its economic benefits when compared to the other materials being used. Literature shows extensive use of graphite in different forms for the removal of organic pollutants such as phenols [77], toluene [78], cresols [79], salicylic acid [80], polyadenylic acid [81], nicotinamide adenine dinucleotide (NADH) [82]. Orori et al. (2010) [83] showed graphite to consume relatively low power in the removal of BOD, COD, TS and metals from pulp and paper effluent. Kong et al. (2009) [84] used a graphite/attapulgite composite for COD removal from textile wastewater, while Bhatnagar et al. (2014) [85] also removed COD and color from the same effluent using graphite electrodes. Methyl orange was degraded using exfoliated graphite electrode by Kong et al. (2012) [86].

Table 2.3: Previous Work on Ammonia Electro-oxidation

Sl. No.	**Anode**	**Cathode**	**Current Density (mA/cm^2)**	**Cl^- (ppm)**	**pH**	**Sample**	**Reference**
1	Graphite	TiO_2	44-110	1,500-3,000	5,7,9	Synthetic	[19]
2	Ti/Pt	Steel	75	4,848	6,7,8,9	Domestic	[72]
3	Ti/Pt coated with Ti/RuO_2-TiO_2	Ti	3	-	-	Domestic	[69]
4	Ti covered with Ti/RuO_2	Steel	50-120	2,000-12,000	5.5-11.5	Powerplant	[70]
5	Ti/RhO_x-TiO_2, Ti/PdO-Co_3O_4, Ti/PbO_2 and Ti/Pt-Ir	Steel	20, 40	5,000	7	Tannery	[67]
6	IrO_2, RuO_2, Pt	Ti	80	10,000	7,12	Synthetic	[65]
7	RuO_2/Ti	Steel	3.8-15.4	0-300	3,7,9.3	Synthetic, domestic	[68]
8	Ti/IrO_2	Steel	3.8-15.4	30-300	5,7,9.3	Synthetic, domestic	[60]
9	Ti/PtO_x–IrO_2	Zr	20	5,800	5.5	Synthetic	[59]
10	BDD	Zr	30	5,800	5,9,11	Synthetic	[73]
11	Ni/$Ni(OH)_2$	Zr	20	37,278	11	Synthetic	[74]
12	Ti-RuO_2–Pt	Ti	5-15	0-5,000	-	Synthetic	[71]
13	BDD	BDD	0.5-5	26,000	11	Aquaculture	[75]
14	Ti/IrO_2-SnO_2-Sb_2O_5	Ti	1-5	25,816	7.5	Aquaculture	[66]
15	Ti/Pt	Steel	-	12,121	7.0	Domestic	[76]

Hunger et al. (1991) [87] employed graphite electrodes for the removal of sulphite ions. Vijayaraghavan et al. (2008) [88] obtained positive results in the removal of COD from shrimp aquaculture wastewater using graphite electrodes.

However, there have only been two reported works on graphite electrodes for the removal of ammonia. The first was on the removal of nitrite and ammonia by Lin and Wu (1996) [19] from saline aquaculture wastewater. They investigated the influence of current, pH, electrolyte conductivity and initial concentrations of ammonia and nitrite. The results obtained by them were better for nitrite removal than for ammonia removal. More than 95% nitrite removal was achieved within 30 minutes with 1.5 A current while ammonia removal was only 15% for the same operational conditions. Applied current density was high (44-110 mA/cm^2). It was also found that increase in conductivity of the electrolyte decreased treatment time and power consumption. Up to 3,000 mg/L sodium chloride was added to improve the conductivity of the water.

Zheng et al.(2009) [89] reported the use of graphite electrodes for ammonia removal from source separated urine. They investigated the effects of current density, ratio of electrode area to solution volume and dilution factor. Though the results were promising, important parameters such as pH and chloride concentration were not investigated.

Therefore there remains scope for further investigation on the use of graphite for ammonia removal, and the influence of these parameters. Moreover, the use of graphite for the electro-oxidation of ammonia has been recommended after

cyclic voltammetric tests by Candido and Gomes (2011) [90]. The erosion of the electrodes is an issue, but it can be overcome in case of waters containing high chloride concentration. Another possible issue may be the relatively low oxygen evolution potential for graphite electrodes, from Table 2.1, which could imply wastage of current.

CHAPTER 3

OBJECTIVES

The electro-oxidation of ammonia from municipal and various industrial effluents has been studied in the recent years. However, not much research has been carried out using graphite electrodes. Their efficiency is well-established in the removal of many organic pollutants. The need for research in this direction has also been recommended on the basis of cyclic voltammetric studies by Candido and Gomes (2011) [90]. The fact that they are relatively less expensive compared to the various other electrodes being investigated for ammonia removal also favors the use of graphite electrodes. Therefore, it is hoped that this study will be a reference for other researchers, describing the advantages of using graphite electrodes for ammonia removal. This study will also try to determine if there are any specific limitations due to which these particular electrodes are not extensively used for ammonia-removal.

The main objective of this study is to investigate the removal of liquid ammonia (non-gaseous) from synthetic wastewater using graphite electrodes by the process

of electro-oxidation.

The specific objectives are:

(1) To establish the optimum conditions of applied current and sodium chloride concentration.

(2) To determine the effect of initial pH on the ammonia removal efficiency.

(3) To determine the effect of varying initial ammonia concentration on ammonia removal efficiency.

(4) To investigate the formation of nitrates during the treatment process.

(5) To calculate power consumption of electro-oxidation treatment for ammonia removal.

CHAPTER 4

MATERIALS AND METHOD

This chapter discusses the apparatus, materials, methods and analysis techniques used in this study to carry out the investigations required to achieve the objectives of this research.

4.1 Preparation of Ammonia Solutions

Synthetic ammonia samples were used for this study. The solutions were prepared using AR grade ammonium sulfate ($(NH_4)_2SO_4$) from Merck in distilled water .

4.2 Preparation of Electrodes

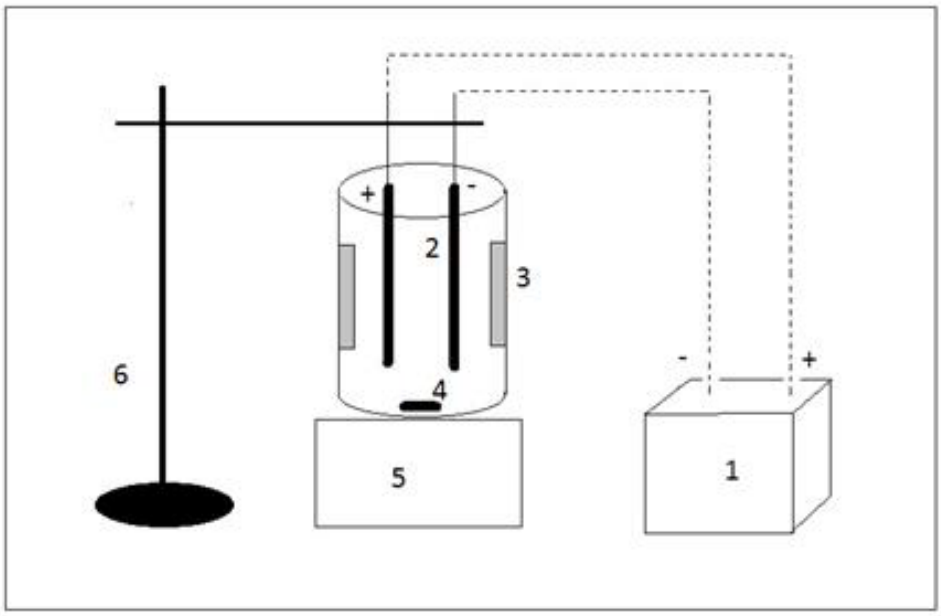
Commercial graphite electrodes were used in this study. The electrodes had dimensions of 120 mm x 100 mm x 5 mm. The electrodes were attached to steel plates for the purpose of fixing to the stand, and connected to the DC supply using crocodile clips. Graphite electrodes were used as anode as well as cathode.

4.3 Experimental setup

The experiments were carried out in a 2 L batch reactor made of Pyrex glass. Baffles were attached to the beaker walls in order to ensure proper mixing. The electrodes were connected to a DC power supply with galvanostatic operational options for controlling the current intensity. The electrodes had a working surface area of 194 cm^2. GP-4303D from EZ Digital Co. Ltd. was the DC supply used, which had a maximum output of 3 A/30 V. A distance of 40 mm between the anode and cathode was maintained for all the experiments in this study. In order to maintain homogeneity of the solution, this setup was placed on a magnetic stirrer and a magnetic bar was used to mix the contents during the experimental runs. Fig.4.1 shows the schematic setup of the electro-oxidation unit, and an actual photograph of the setup is shown in Fig.4.2.

4.4 Design of experiments

Four sets of experiments were conducted. The first set of experiments was conducted in order to establish the optimum values of applied current and NaCl concentration for ammonia removal. The second set of experiments was conducted to observe the effect of initial pH on the ammonia removal efficiency. In the third set of experiments, the effect of varying initial ammonia concentrations on the ammonia removal efficiency was studied. The fourth set of experiments was carried out to determine the effect of higher NaCl concentrations on ammonia removal.



1. D.C. Power supply
2. Graphite electrodes
3. Glass beaker with baffles
4. Magnetic bar
5. Magnetic stirrer
6. Iron stand for electrodes

Figure 4.1: Schematic setup of Electro-oxidation Unit

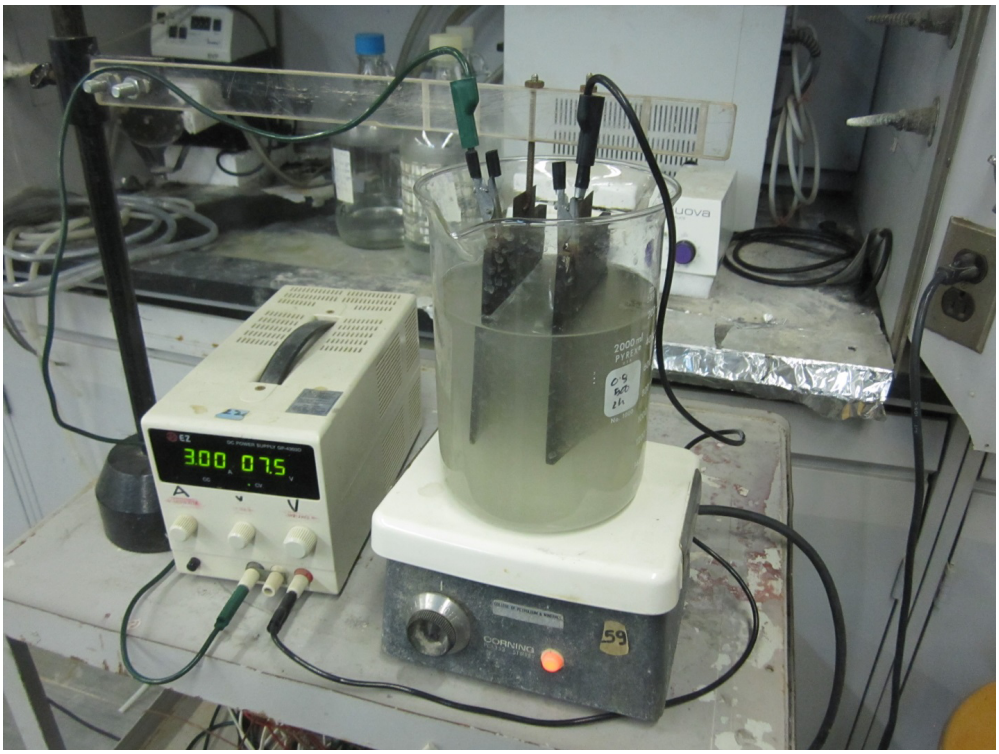


Figure 4.2: Photograph showing actual experimental setup

4.4.1 Determination of Optimum Current and Sodium Chloride concentration

The first phase of experiments was aimed at establishing optimum values of applied current and sodium chloride concentration for ammonia removal. Optimum here is defined as those conditions that enable highest ammonia removal in shortest time. Power consumed was not considered while determining the optimum conditions.

The experiments were carried out employing six different values of applied current, ranging from 0.5 A to 3.0 A, and four different concentrations of sodium chloride, from 2,500 mg/L to 10,000 mg/L. The experimental design for the first set of experiments is given in Table 4.1. Sodium chloride concentration of 1000 mg/L was excluded from the experimental design after preliminary studies found no TAN removal. Moreover the low conductivity of the electrolyte led to rapid fouling of the electrode. Very high potential had to be applied to pass current, which was another reason for eliminating the experiments at 1,000 mg/L NaCl concentration.

40 mg/L TAN (Total Ammonia Nitrogen) samples were prepared using ammonium sulfate at an unadjusted initial pH (6.8). Sampling was done at 0, 5, 10, 20, 30, 50, 70, 90, 110 and 130 minutes. TAN of the samples was measured using ammonia ion-selective electrode. pH of the collected samples was also measured. From the suggested set of 24 experiments, the best combination of the two parameters, viz., sodium chloride concentration and applied current, was determined in

terms of ammonia removal efficiency.

Table 4.1: Determination of Optimum Current and Sodium Chloride concentration

Current	**NaCl concentration (mg/L)**			
(A)	**2,500**	**5,000**	**7,500**	**10,000**
0.5	A1	A2	A3	A4
1.0	B1	B2	B3	B4
1.5	C1	C2	C3	C4
2.0	D1	D2	D3	D4
2.5	E1	E2	E3	E4
3.0	F1	F2	F3	F4

4.4.2 Effect of initial pH on the removal efficiency of ammonia

In order to determine the effect of initial pH of the solution on the removal efficiency of ammonia, tests were carried out at the optimum conditions as determined in section 4.4.1, by adjusting the initial pH of the solution to 1, 2, 3, 4, 5 and 9. pH was increased or decreased by the addition of NaOH or HCl respectively. The design of experiments for this phase is shown in Table 4.2. Since the pH of the ammonium sulfate solution prepared was 6.8 without adjustment, this was used as neutral pH. Moreover, pH was not controlled during the experimental runs.

Table 4.2: Effect of Initial pH on the Removal Efficiency of Ammonia

Experiment No.	**Applied Current (A)**	**NaCl concentration (mg/L)**	**Initial pH**
P1	Optimum Value from first set of experiments (Table 4.1)	Optimum Value from first set of experiments (Table 4.1)	9
P2			6.8 (Unadjusted)
P3			5
P4			4
P5			3
P6			2
P7			1

4.4.3 Effect of varying initial ammonia concentration on ammonia removal efficiency

Ozyonar et al. (2012) [4] reported industrial effluents with ammonia concentrations as high as 2500 mg/L. Therefore the effect of higher initial ammonia concentrations on the removal efficiency was also studied. After initial experiments with 40 mg/L TAN (in section 4.4.1 and 4.4.2), investigations thereafter continued with 100, 200, 400 and 600 mg/L TAN as shown in Table 4.3.

Table 4.3: Effect of varying initial ammonia concentration on ammonia removal efficiency

Experiment No.	**Applied Current (A)**	**NaCl concentration (mg/L)**	**TAN concentration (mg/L)**
N1	Optimum Value from first set of experiments (Table 4.1)	Optimum Value from first set of experiments (Table 4.1)	40
N2			100
N3			200
N4			400
N5			600

4.4.4 Effect of higher sodium chloride concentration on ammonia removal

Effluents from some industries are known to have chloride concentration of up to 26,000 mg/L (Diaz et al., 2011) [75]. Therefore, high NaCl concentrations of 20,000, 30,000 and 50,000 mg/L were also explored for the optimum conditions of applied current established from the first set of experiments. The experimental design for this phase is presented in Table 4.4.

Table 4.4: Effect of higher sodium chloride concentration on ammonia removal

Experiment No.	**Applied Current (A)**	**NaCl concentration (mg/L)**
S1	Optimum Value from first set of experiments (Table 4.1)	10,000
S2		20,000
S3		30,000
S4		50,000

4.5 Analysis

Ammonia concentration of the solution was determined following APHA method 4500-NH_3 D, given in the Standard Methods for the Examination of Water and Wastewater (21st edition, 2005.) [91]. Orion 95-12 ammonia electrode connected to a Thermo Scientific millivolt meter was used for ammonia and WTW 3310 meter was used for pH measurements. Dionex ICS-3000 was used for ion chromatography to analyze nitrate.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Determination of Optimum Current and Sodium Chloride concentration

The effect of varying the applied current on TAN removal at different initial sodium chloride concentrations is depicted in Fig.5.1-5.4. Fig.5.1 shows that at an initial sodium chloride concentration of 2,500 mg/L, no TAN removal was observed at currents of 0.5 and 1.0 A even after 130 minutes of treatment. However, a further increase in applied current showed gradual TAN removal. An applied current of 1.5 A showed 5.6% removal after 20 minutes, followed by a linear increase in TAN removal, with 25.5% removal achieved after 130 minutes. Further increase in applied current showed higher TAN removal, with 28.9% and 32.2% TAN removed by applied currents of 2.0 and 2.5 A after 130 minutes respectively. Current of 3.0 A showed highest TAN removal (35.3% after 130 minutes).

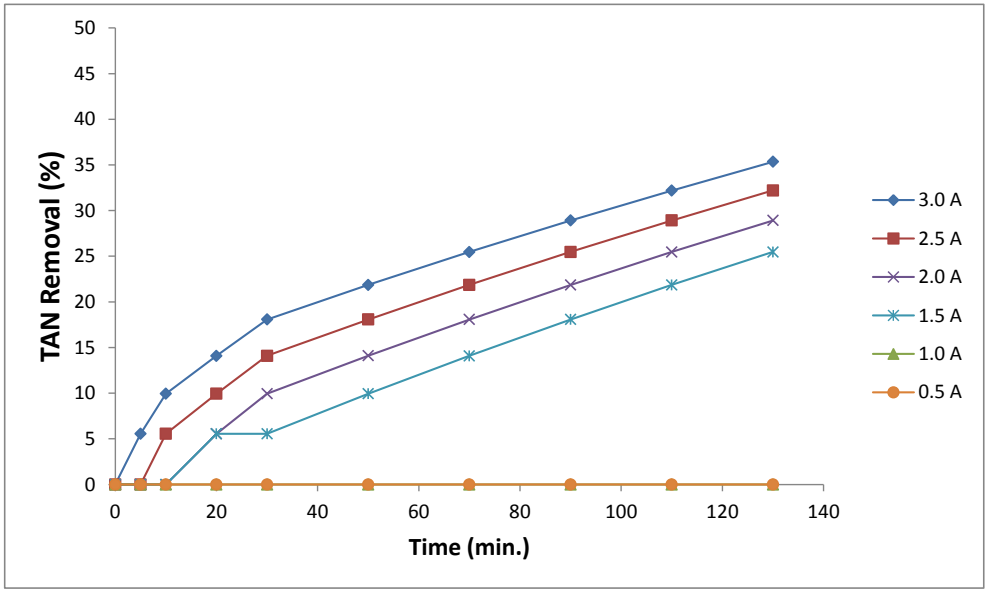


Figure 5.1: Variation of TAN removal with applied current in samples with initial 2,500 mg NaCl/L

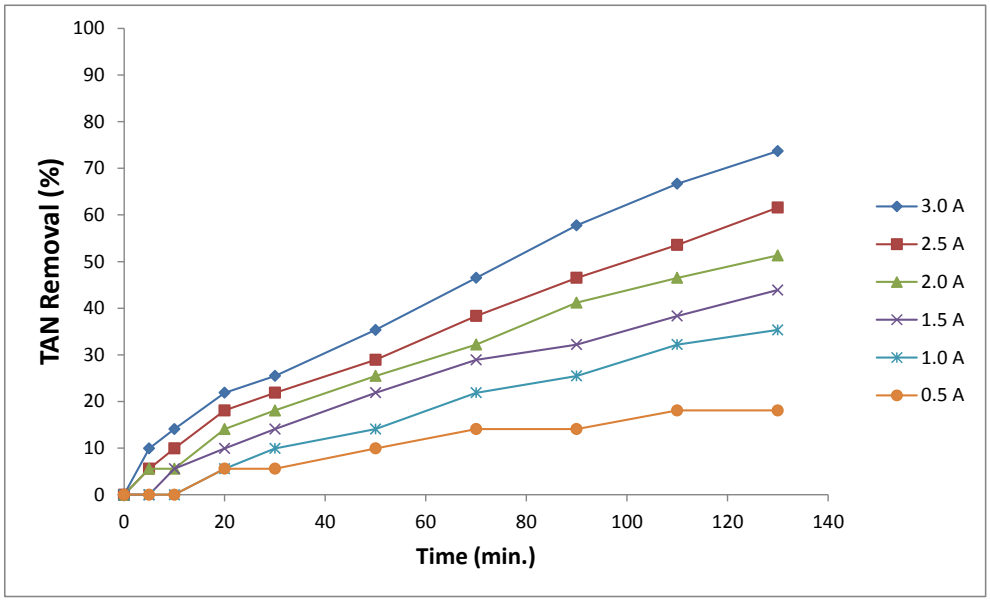


Figure 5.2: Variation of TAN removal with applied current in samples with initial 5,000 mg NaCl/L

These results show that increasing the applied current increases TAN removal. This can be explained by the indirect mechanism of ammonia electro-oxidation which proceeds by the formation of hypochlorous acid (equations 2.4-2.8). For present study, it was established by preliminary experiments that ammonia removal was by the indirect mechanism. There was no TAN removal from samples containing high concentrations (10,000 mg/L) of sodium fluoride and sodium bromide, while similar concentration of sodium chloride showed quick TAN removal. This can be explained by the presence of chloride which enables formation of chlorine gas and hypochlorous acid, thereby leading to ammonia oxidation by the indirect mechanism. However, in the absence of chloride, ammonia was not removed. The probability of direct mechanism being involved in ammonia removal in present study was thus eliminated.

Hypochlorous acid acts as the oxidizing agent, and its generation (equation 2.5) takes place only after the evolution of chlorine gas at the anode (equation 2.4), in which it can be observed that electrons play a significant role in the reaction. When current is increased, the physical meaning is that more electrons are supplied to the system. This facilitates the evolution of chlorine gas and the subsequent generation of hypochlorous acid. In our case, at low currents of 0.5 and 1.0 A, the current was not sufficient to enable the formation of chlorine gas, which in turn prevented the generation of hypochlorous acid. Thus, there was no TAN removal observed at low currents (0.5 and 1.0 A). However, as the current was increased, there was adequate formation of chlorine gas and as a result,

hypochlorous acid was generated, which led to TAN removal. The generation of hypochlorous acid was proportional to the applied current, therefore the application of higher current showed greater TAN removal. This is in agreement with the reports by Vanlangendonck et al. (2005) [70] using Ti/RuO_2 anode, Szpyrkowicz et al. (2005) [67] using three different combinations of Ti anodes, Li and Liu (2009) [68] using Ti/RuO_2 and Diaz et al. (2011) [75] using BDD anode.

The sodium chloride concentration was then increased to 5,000 mg/L and the results are shown in Fig.5.2. It can be observed that an applied current of 0.5 A removed only 18.1% TAN after 130 minutes compared to 35.3% TAN removal at 1.0 A. When the current was increased to 1.5, 2.0, 2.5 and 3.0 A, the TAN removal after 130 minutes increased to 43.9%, 51.3%, 61.6% and 73.7% respectively. Increasing current resulted in an increase in the TAN removal. This is in agreement with the findings in Fig.5.1 for sodium chloride concentration of 2,500 mg/L. It is also noteworthy that in all cases of applied current, TAN removal at NaCl concentration 5,000 mg/L is higher than the corresponding values for NaCl concentration 2500 mg/L (Fig.5.1). When the NaCl concentration was increased from 2,500 to 5,000 mg/L, TAN removal after 130 minutes increased from 0 to 18.1%, 0 to 35.3%, 25.5 to 43.9%, 28.9 to 51.3%, 32.2 to 61.6% and 35.3 to 73.7% for currents 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 A respectively. This clearly signifies that increase in chloride concentration enhances ammonia removal, which conforms to the indirect mechanism of ammonia removal. Chen (2004) [28], Vanlangendonck et al. (2005) [70], Anglada et al. (2009) [56] and Li and Liu (2009) [68] also reported

that increasing chloride concentration enhances ammonia removal by the indirect mechanism.

The same trends can be observed for 7,500 mg/L NaCl in Fig.5.3 where 0.5 A current removed only 28.9% TAN after 130 minutes, but increasing the current increased TAN removal. TAN removal of 46.5%, 55.7%, 68.2%, 87.7% and 95.0% were observed for current 1.0, 1.5, 2.0, 2.5 and 3.0 A respectively after 130 minutes. Increase in applied current consistently showed greater TAN removal. TAN removal was higher than the corresponding removal for NaCl concentration 5,000 mg/L (Fig.5.2), again signifying that increase in chloride concentration favors TAN removal.

At NaCl concentration 10,000 mg/L (depicted in Fig.5.4), similar TAN removal characteristics were noticed. TAN removal increased with increase in applied current, from 35.3% at 0.5 A after 130 minutes to 61.6%, 79.2%, 89.8%, 98.3% and 99.2% at 1.0, 1.5, 2.0, 2.5 and 3.0 respectively. These TAN removal values are also higher than the corresponding removal at 7,500 mg NaCl/L (Fig.5.3).

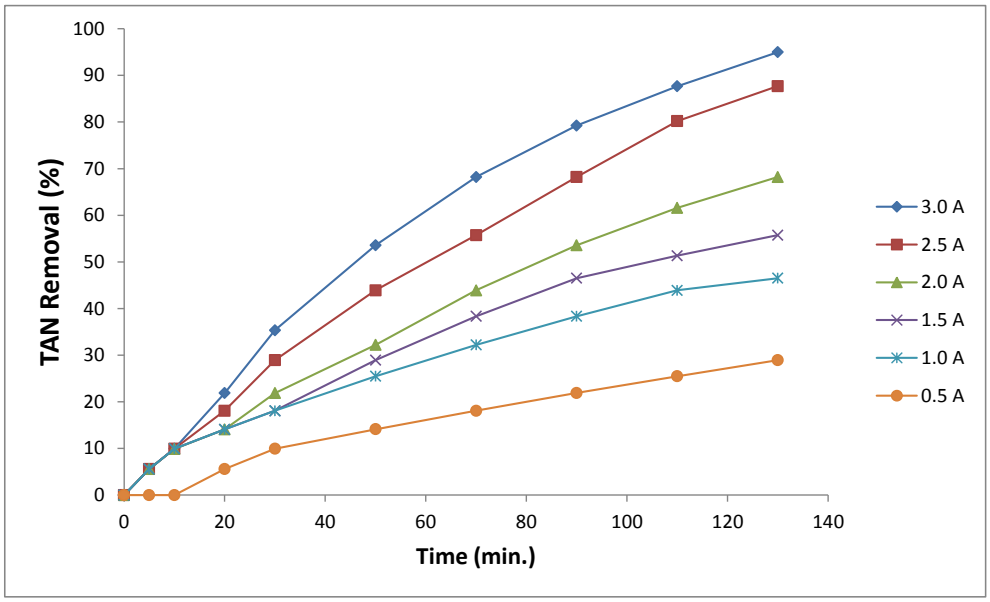


Figure 5.3: Variation of TAN removal with applied current in samples with initial 7,500 mg NaCl/L

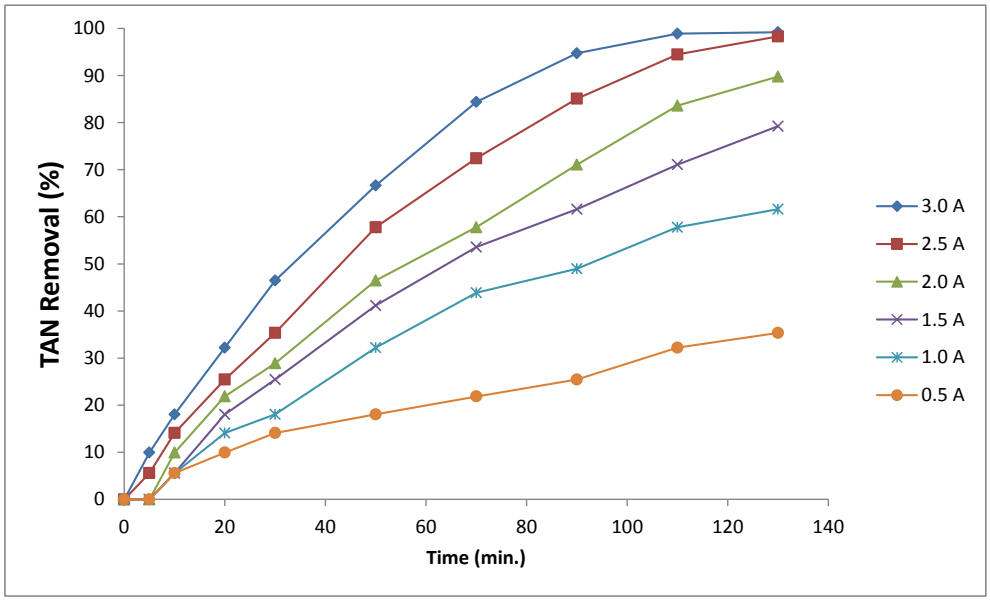


Figure 5.4: Variation of TAN removal with applied current in samples with initial 10,000 mg NaCl/L

For a better observation of the effect of sodium chloride concentration on TAN removal, a plot was made to compare TAN removal by varying NaCl concentration at a constant current of 3.0 A (Fig.5.5). It was noticed that at 2,500 mg NaCl/L, TAN removal after 130 minutes was 43.9%. When NaCl concentration was increased to 5,000 mg/L, TAN removal increased to 73.7%. Further increase in NaCl concentration to 7,500 and 10,000 mg/L resulted in TAN removal of 95.0% and 99.2% respectively. This corroborates the fact that increase in chloride concentration favors TAN removal.

Another plot was constructed (Fig.5.6) using TAN removal at 90 minutes for all the explored combinations of current and NaCl concentration. The sampling time of 90 minutes was chosen because complete TAN removal (99.2%) was achieved by 90 minutes at the most favorable conditions of current (3.0 A) and sodium chloride concentration (10,000 mg/L). This figure makes it clear that the fastest removal of TAN is achieved by combining the highest applied current with highest NaCl concentration, thereby making them the optimum operational parameters for present study.

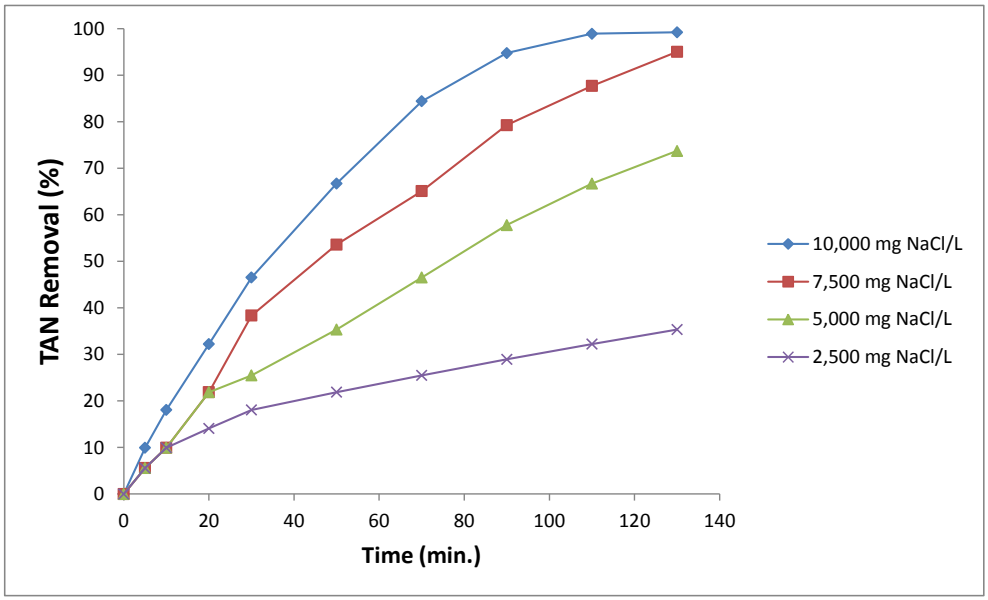


Figure 5.5: Variation of TAN removal with NaCl concentration at 3.0 A current

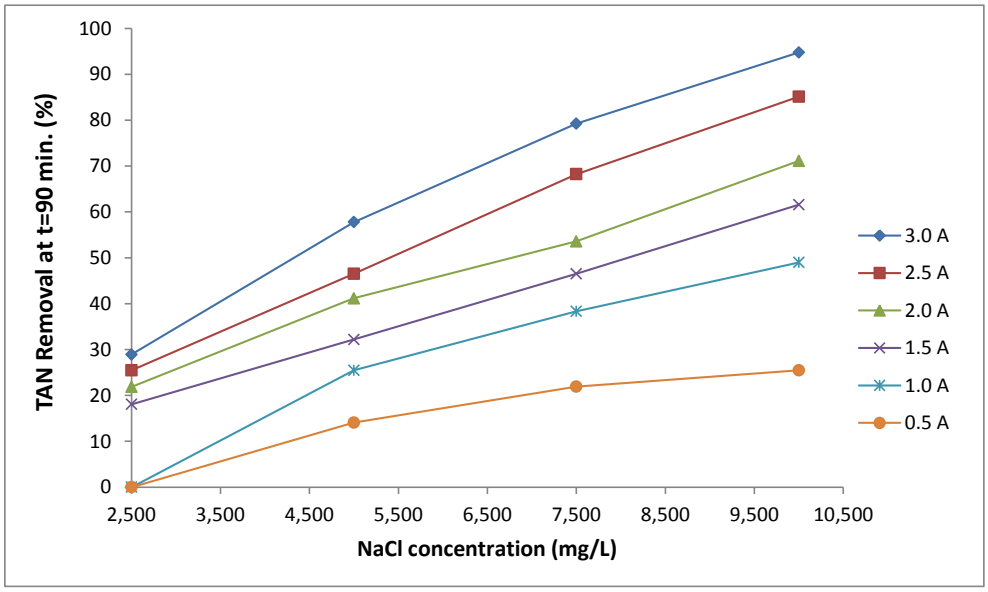


Figure 5.6: Variation of ammonia removal with NaCl concentration after 90 minutes

5.1.1 Observations

During these experiments, formation of bubbles at both the cathode and anode was observed. Electrode fouling was also observed at lower NaCl concentrations of 1,000 and 2,500 mg/L, which is because of the low conductivity of the electrolyte. Kapalka et al. (2010) [74] also observed a similar phenomenon for $Ni/Ni(OH)_2$ electrodes. This could be one of the limitations of graphite and other electrodes at lower electrolyte concentration (NaCl) which may have corroded the electrode. The fouling was predominantly at the anode.

Fig.5.7 shows the black color of the sample after just 10 minutes of treatment of sample containing 2500 mg NaCl/L. However in Fig.5.8, there is no fouling of the electrode even after 75 minutes of treatment at 7,500 mg NaCl/L, which signifies the dependency of this treatment on the chloride content.

Figure 5.7: Photograph showing electrode fouling for sample with 2500 mg NaCl/L, 1.5 A after 10 minutes of treatment

Figure 5.8: Photograph showing experiment using sample having 7500 mg NaCl/L, 2.5 A after 75 minutes of treatment

5.2 Effect of Initial pH

Fig.5.9 shows the TAN removal for sample solutions with initial pH adjustments. It can be observed that at pH 1, the TAN removal is significantly faster than all other pH. TAN removal of 96.0% was observed after 50 minutes. The corresponding TAN removal for samples with other pH values, which show 65-75% removal, are much slower compared to pH 1. There is no significant trend for the other pH (2, 3, 4, 5, 6.8 and 9).

The reason for this quick TAN removal at pH 1 can be explained. It should be noted that the initial pH adjustments were made by adding NaOH or HCl to raise or lower the pH respectively. For the sample with initial pH 1, more than 10 ml of concentrated HCl was added to lower the pH to the required level. When HCl is added to the solution, it dissociates to form Cl^- (chloride) ion. The density of conc. HCl added was 1.19 g/ml, therefore an addition of 10 ml of conc. HCl to the sample having volume 1.5 L signifies an addition of roughly 7 g/L (or 7,000 mg/L) chloride. This is much higher than chloride concentrations of all other samples. Such a high chloride concentration enables very quick evolution of chlorine gas and subsequent generation of HOCl, the ammonia-oxidizing agent. Hence the quick TAN removal at pH 1. Although varying amounts of conc. HCl were added to all samples with initial pH 2-5, the volume added in all those cases were much lower compared to that for pH 1.

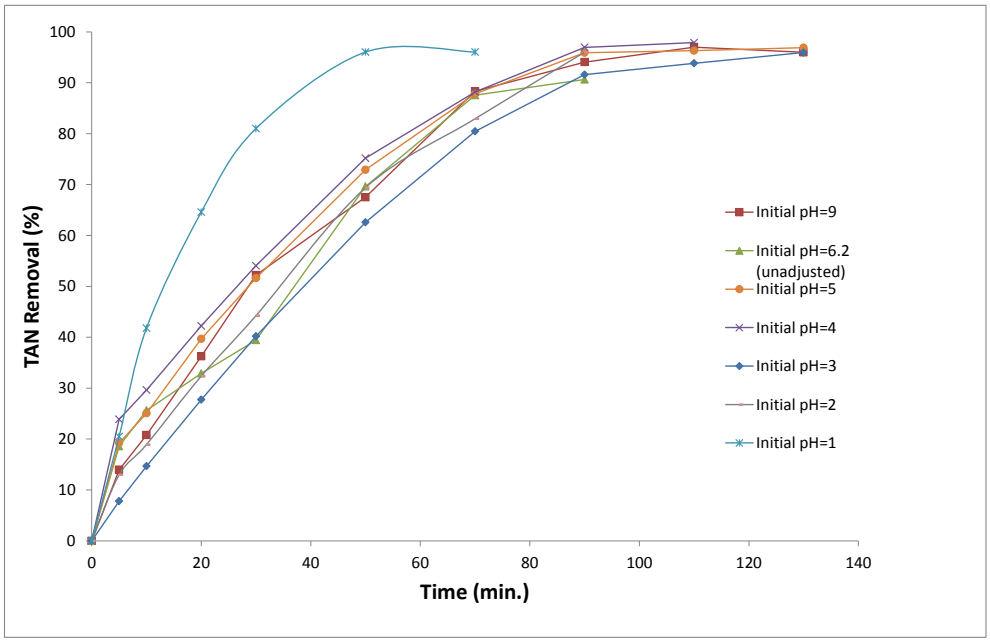


Figure 5.9: Effect of initial pH on TAN removal at 10,000 mg NaCl/L, 40 mg TAN/L and 3.0 A applied current

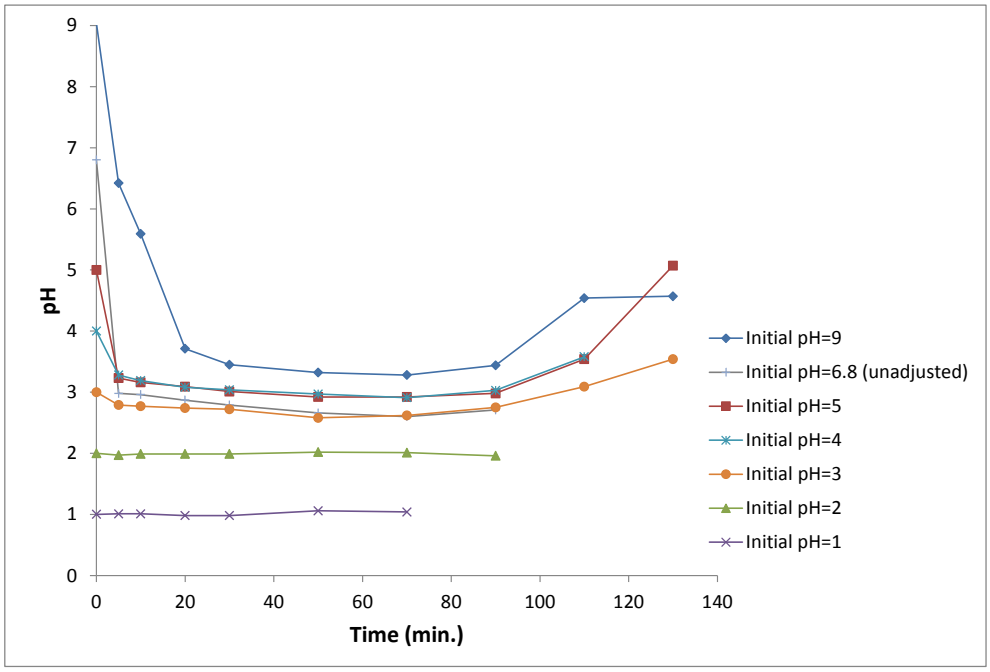


Figure 5.10: Variation of pH during experiments for samples with different initial pH, at 10,000 mg NaCl/L, 40 mg TAN/L, and 3.0 A current

Fig.5.10 shows the pH variation over time for each experiment. All samples showed a drastic fall in pH even within 5 minutes. This is clearly seen for all samples except for pH 1 and 2 which are already very low. Lin and Wu (1996) [19] also reported a similar behavior. Sample with initial pH 9 drops to 6.4 after 5 minutes, whereas pH values for samples with initial pH 6.8, 5, 4 and 3 dropped to 3.0, 3.2, 3.3 and 2.8 respectively. This drop in pH can be attributed to the generation of HCl from the reactions involved in HOCl formation from chlorine gas (equation 2.5) and ammonia oxidation by HOCl (equations 2.6 - 2.8). Since HCl is a strong acid, it causes reduction in pH in most of the samples. However, in the case of samples with pH 1 and 2, the pH is already so low that the production of more HCl does not affect their pH. The pH of those samples (especially for pH 1 and pH 2) were initially adjusted to such highly acidic level by the addition of HCl.

This decline in pH was followed by a period of stability and then a gradual increase. In order to these explain pH variations, TAN removal and pH was combined in the same plot against time. Plots were constructed for each pH value starting from 3 to 9, and have been presented as Fig.5.11-5.15. pH 1 and pH 2 were not plotted this way since they did not show these pH variations. From Fig.5.11, it can be noticed that the pH remains constant around 3, and when the TAN removal reaches 90% (after 70 minutes), the pH increases gradually. The same observation can be made from Fig.5.12-5.15.

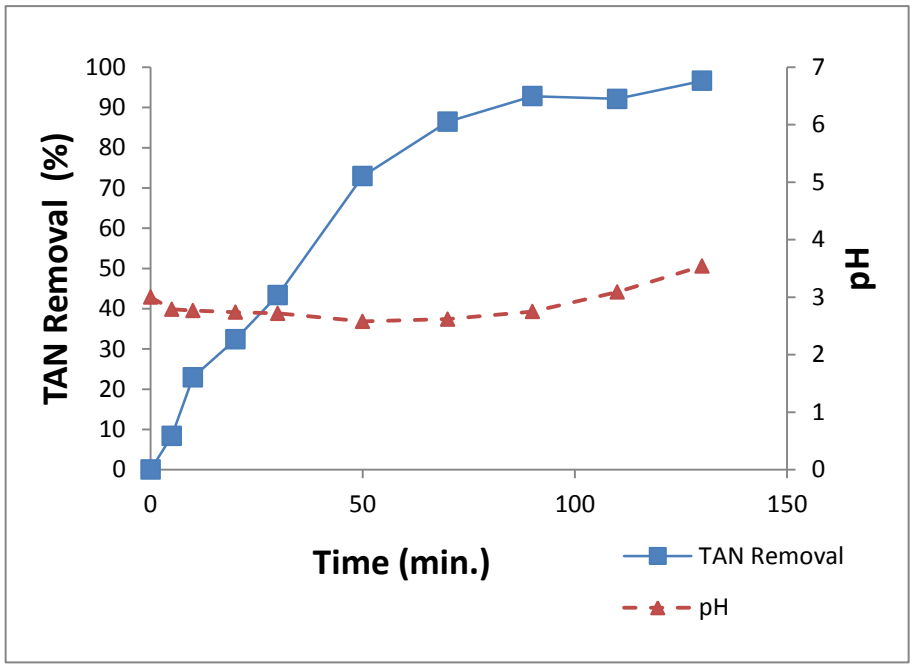


Figure 5.11: TAN removal and pH variation for sample with initial pH=3, 10,000 mg NaCl/L, 40 mg TAN/L, 3.0 A current

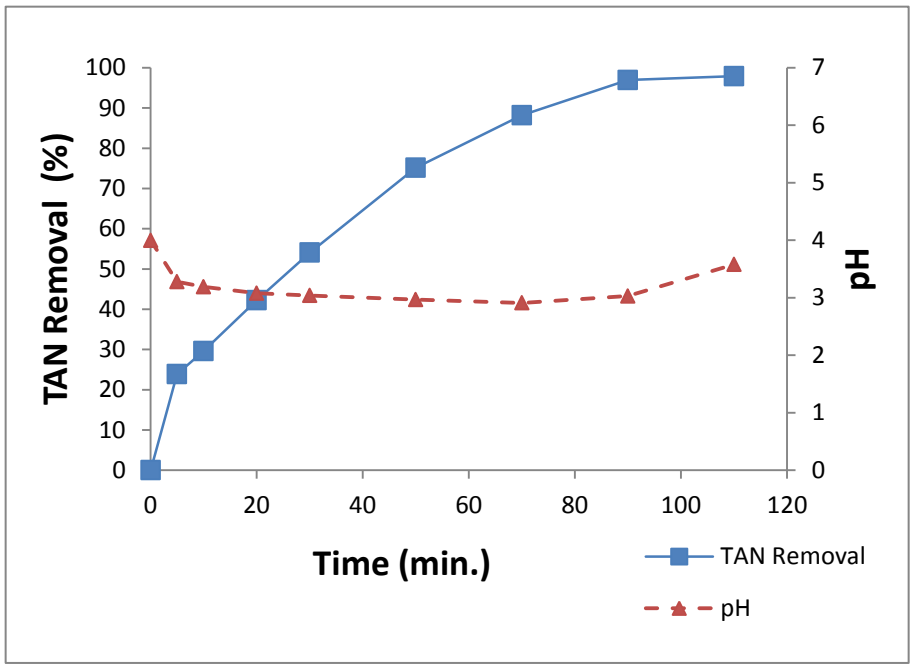


Figure 5.12: TAN removal and pH variation for sample with initial pH=4, 10,000 mg NaCl/L, 40 mg TAN/L, 3.0 A current

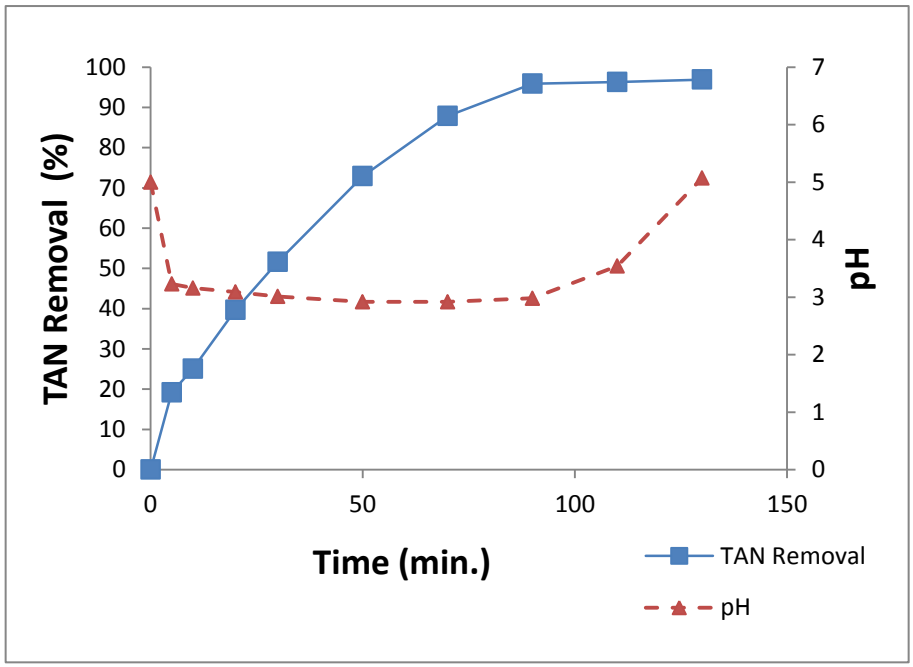


Figure 5.13: TAN removal and pH variation for sample with initial pH=5, 10,000 mg NaCl/L, 40 mg TAN/L, 3.0 A current

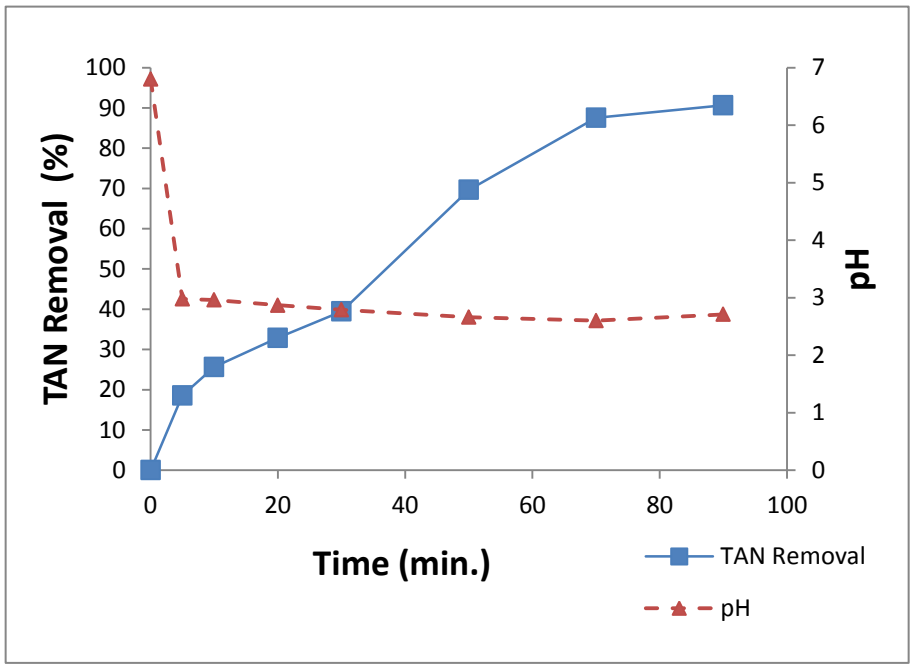


Figure 5.14: TAN removal and pH variation for sample with initial pH=6.8, 10,000 mg NaCl/L, 40 mg TAN/L, 3.0 A current

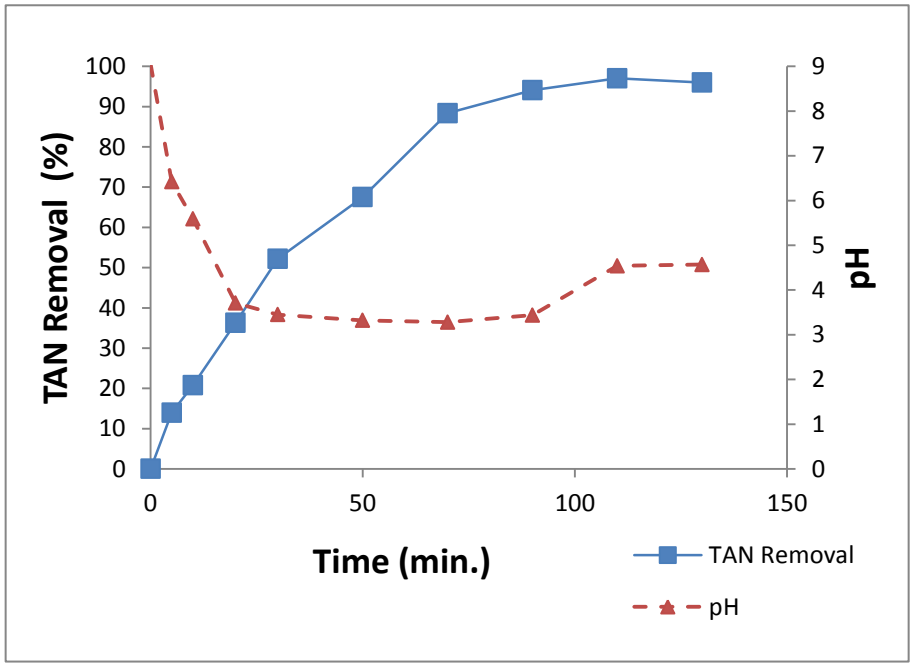


Figure 5.15: TAN removal and pH variation for sample with initial pH=9, 10,000 mg NaCl/L, 40 mg TAN/L, 3.0 A current

From these graphs, it is evident that when the TAN removal is near completion, the pH starts increasing gradually. This phenomenon was not found discussed in available literature. In order to explain this phenomenon, it is necessary to first understand the system and the reactions that occur therein. The components of the system are mainly sodium chloride and ammonia. Equation 5.1 is the overall reaction occurring in the system:

$$2NaCl + 2H_2O \rightarrow H_2(g) + Cl_2(g) + 2NaOH \tag{5.1}$$

From equation 5.1, the NaOH formed tends to increase the pH of the solution. However, the HCl formed during the process (equations 2.5 - 2.8) counteracts this pH increase and maintains a steady pH. HOCl is formed, which reacts with ammonia and ammonium ion, converting them to nitrogen gas (N_2) and nitrates (NO_3^-)(equations 2.6-2.8). This explains the TAN removal. As long as there is enough TAN in the system to react with HOCl, the pH remains steady because HCl is continuously generated during the ammonia degradation reaction.

It should be noted that the formation of HOCl from chlorine gas (equation 2.5) is a reversible reaction that proceeds to the left (combination of HOCl and HCl to form chlorine gas) at pH below 4. When nearly all of the TAN is exhausted, HOCl is not utilized to oxidize ammonia anymore, thereby leading to an increase in HOCl concentration within the system. According to the Le Chatelier principle, if a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium shifts to counteract the change to re-establish an equilibrium. In

this case, the existing equilibrium in the HOCl generation reaction is disturbed by the increase in HOCl concentration. This increase in HOCl concentration shifts the equilibrium towards the reverse reaction. This gradually reduces the concentration of HOCl and HCl (reactants in this reverse reaction), while the NaOH concentration is continuously increasing regardless of these changes (equation 5.1). Hence the solution pH increases.

In conclusion, it can be stated that initial pH seems to have no effect on the removal of TAN. The quick TAN removal observed for pH 1 was due to the high chloride content rather than the effect of pH. Highly basic conditions were not studied because the conversion of ammonium ion to ammonia gas in those conditions is well known [91]. It has also been reported by Vanlangendonck et al. (2005) [70] and Li and Liu (2009) [68] that at high pH values the chlorate (ClO_3^-) formation mechanism competes with HOCl for the available chlorine, thereby affecting TAN degradation adversely.

5.3 Effect of varying initial ammonia concentration on ammonia removal

Fig.5.16 shows TAN removal from samples with varying initial TAN concentration at constant current of 3.0 A and 20,000 mg NaCl/L. It can be observed that the sample with lowest initial TAN concentration (40 mg/L) showed 49.0% TAN removal after 20 minutes, and 97.9% after 30 minutes. TAN removal of 93.9%

was achieved from sample with 100 mg/L initial TAN after 90 minutes. This treatment time is longer than that required by the sample with 40 mg/L initial TAN, which is due to higher TAN content. When the TAN of the sample is higher, more hypochlorous acid is required to oxidize the ammonia. The longer treatment time, therefore, is due to the longer time period required to generate this higher quantity of hypochlorous acid. The same applies to the samples with further higher initial TAN concentrations of 200, 400 and 600 mg/L, which showed only 81.1%, 54.5% and 42.1% respectively after 130 minutes. Linear trend is followed by TAN removal in all cases, although the sample with 100 mg/L initial TAN content does not follow this trend when TAN removal is near completion (from 93.9% onwards). This is since the reaction follows pseudo zero-order kinetics, which is explained as follows.

These results for samples with varying initial TAN concentrations are expressed better in terms of residual TAN (Fig.5.17). Since the TAN concentration varies linearly with time, it can be stated that TAN removal follows zero-order kinetics for all cases studied. Zero-order reactions are those where the reaction rate is independent of the concentration of reactants. This is similar to the observations by Vanlangendonck et al. (2005) [70] and Li and Liu (2009) [68], although Szpyrkowicz et al.(2005) [67] observed a pseudo first-order trend. Since our process follows zero-order reaction, or pseudo zero-order reaction, the implication is that the rate of reaction is not affected by the ammonia concentration.

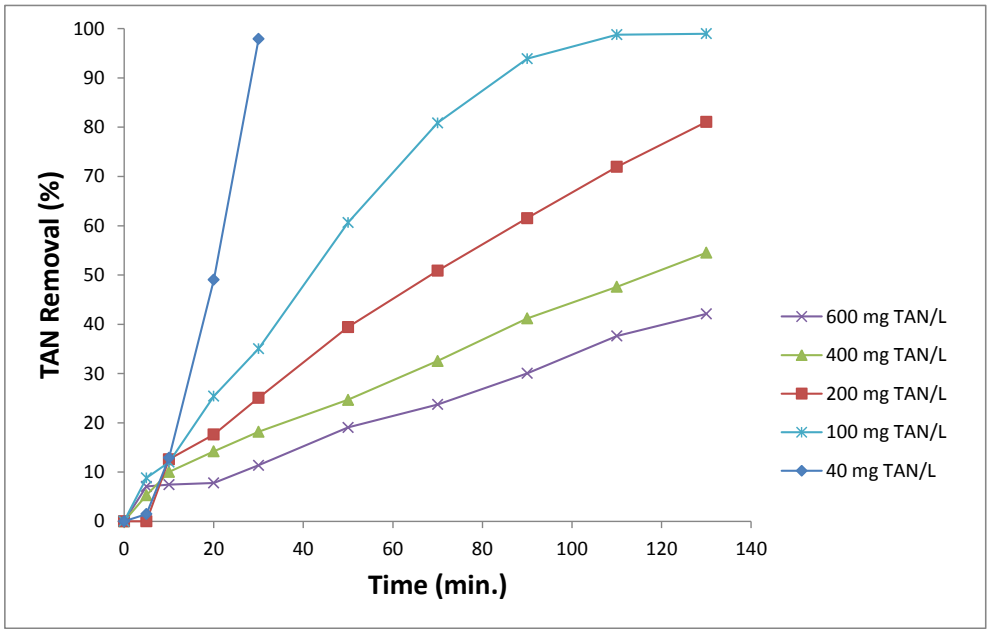


Figure 5.16: TAN removal for samples with varying initial TAN concentration at 20,000 mg NaCl/L and 3.0 A current

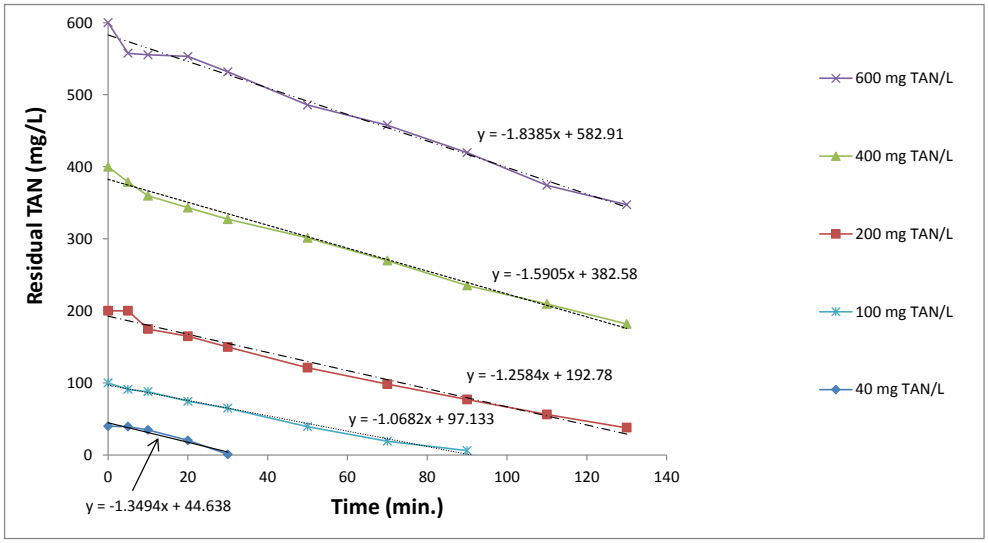


Figure 5.17: Residual TAN for samples with varying initial TAN concentration at 20,000 mg NaCl/L and 3.0 A current

The rate of HOCl production is the controlling factor, which is in turn dependent on the rate of chlorine gas evolution at the anode (equation 2.4). However, a zero-order reaction is independent of concentration of reactants only up to a point, after which a different rate law is followed. This is because the concentration of the reactants becomes so low that it cannot follow zero-order rate law anymore. The rate of reaction is affected by the unavailability of reactant, which is ammonia in this case. This is the reason why this is also known as pseudo zero-order rate law.

From Fig.5.17, it can be seen that for the sample with 40 mg/L initial TAN, only 0.8 mg/L TAN remains after 30 minutes of treatment. However, for samples with higher initial TAN concentrations of 100, 200, 400 and 600 mg/L, the residual TAN values were 64.9, 149.9, 327.2 and 531.7 mg/L respectively. The samples with initial TAN concentrations 200, 400 and 600 mg/L did not reach discharge standards even after 130 minutes of treatment, with residual TAN values 37.8, 181.8 and 347.3 mg/L respectively. However, linear trend was observed for all samples and the equation for each is given in the plot. These linear equations can be used to estimate the treatment time required for each sample to reach discharge standards. Assuming a discharge standard of 1 mg/L TAN, the time required to treat the samples with initial TAN concentrations of 200, 400 and 600 mg/L can be calculated as 2.5, 4.0 and 5.3 hours respectively.

5.4 Effect of higher sodium chloride concentration on ammonia removal

From Fig.5.18, TAN removal is slowest for sample with NaCl concentration 10,000 mg/L and fastest for sample with NaCl 50,000 mg/L. After 20 minutes, the TAN removal for sample with 10,000 mg/L NaCl concentration was only 32.2%, whereas samples with 20,000, 30,000 and 50,000 mg/L NaCl concentration showed 49.0%, 90.9% and 98.4% TAN removal respectively. There is a much quicker TAN removal observed in the samples with NaCl concentrations 30,000 and 50,000 mg/L when compared to the ones with lower concentration. Thus it can be concluded that the same trend of ammonia removal seen in Section 5.1 continues even at much higher NaCl concentration. With the increase in NaCl concentration, an increase in ammonia removal was observed. This can be attributed to the quicker rate of chlorine gas evolution as the chloride content of the sample increases. As explained in Section 5.3, it is the rate of evolution of chlorine gas at the anode that determines the rate of reaction and consequently, ammonia removal.

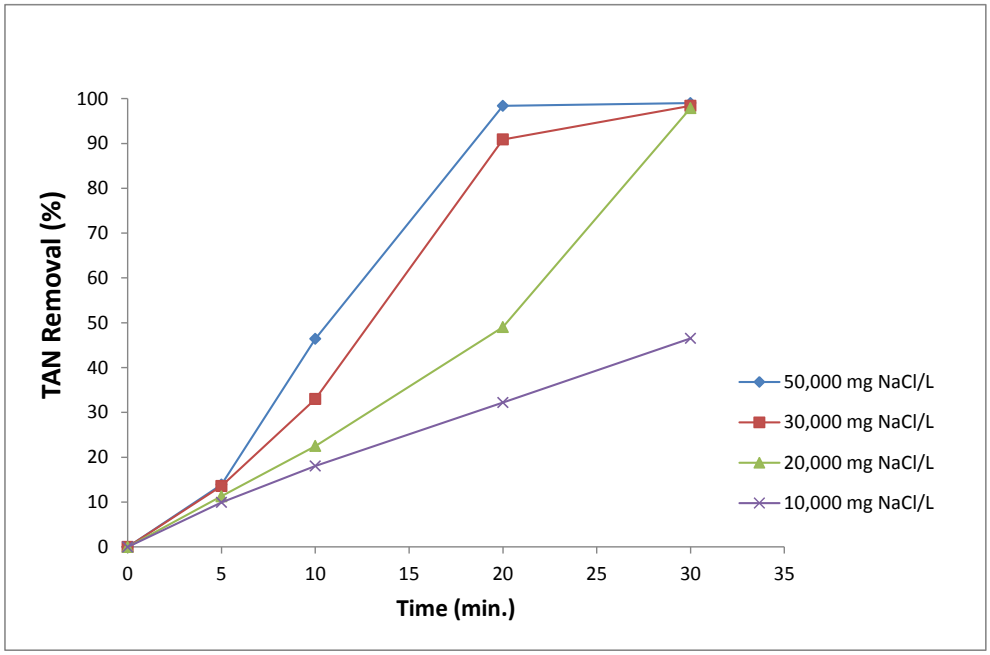


Figure 5.18: Variation of TAN removal in samples with higher NaCl concentration at 40 mg TAN/L and 3.0 A current

5.5 Formation of Nitrates

Plots were made of ammonia, nitrate and total nitrogen against time for three samples in order to study the formation of nitrates during the TAN removal process. The Total Nitrogen is the sum of nitrate-N and TAN since there were no nitrites detected. The phenomenon of nitrate production can be explained by the equation 5.2 which explains how a portion of the ammonia is converted to nitrate.

$$HOCl + (1/4)NH_4^+ \rightarrow (1/4)NO_3^- + (1/4)H_2O + (3/2)H^+ + Cl^- \qquad (5.2)$$

[Source: Liu et al.(2009) [60]]

Though equations 2.6 and 2.7 show how HOCl reacts with ammonia and ammonium ion respectively to release nitrogen gas, there is another possible side-reaction (equation 5.2) which shows that nitrates may also be produced during the reaction of HOCl with ammonium ion.

This is confirmed by the plots in Fig.5.19-5.21, which show that the steady fall in TAN is accompanied by a gradual but non-negligible increase in the nitrate level. For initial TAN 40 mg/L (Fig.5.19), the nitrate level after 90 minutes was found to be 6.9 mg/L, while for TAN concentration 100 (Fig.5.20) and 200 mg/L (Fig.5.21), it was 15.8 and 18.1 mg/L respectively after 90 minutes. These can be expressed as 0.19, 0.17 and 0.15 mg nitrate/mg TAN removed, respectively. It is significant to monitor the nitrate levels for treated effluents because they

are also pollutants. However, the regulatory limits for nitrates in wastewater are significantly higher than those for ammonia. Considering a nitrate discharge standard of 50 mg/L [92], the method proposed by present study can be used to treat wastewater with ammonia concentrations upto 250 mg/L. Vlyssides et al. (2002) [72] reported nitrate levels of 0.06-0.79 mg/mg TAN removed, the values being inversely proportional to pH. Kapalka et al. (2010) [74], using nickel electrodes, reported a nitrate release of 0.43 mg/mg TAN removed.

5.6 Energy consumption of electro-oxidation treatment

Energy consumption is another major factor in the electro-oxidation process. Vlyssides et al. (2002) [72] reported that the power consumption for electro-oxidation treatment is ten times that of conventional biological treatment. However, it is very difficult to make comparisons between different technologies since these estimates for energy requirements are based on different assumptions, and as a result the energy estimates could vary considerably [76].

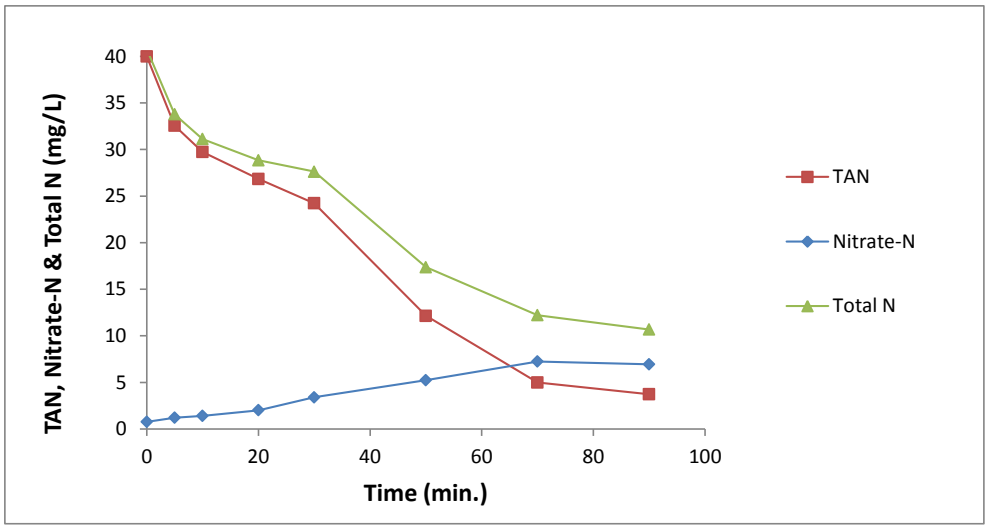


Figure 5.19: TAN removal, nitrate N and Total N in sample with initial 40 mg TAN/L, 10,000 mg NaCl/L at 3.0 A current

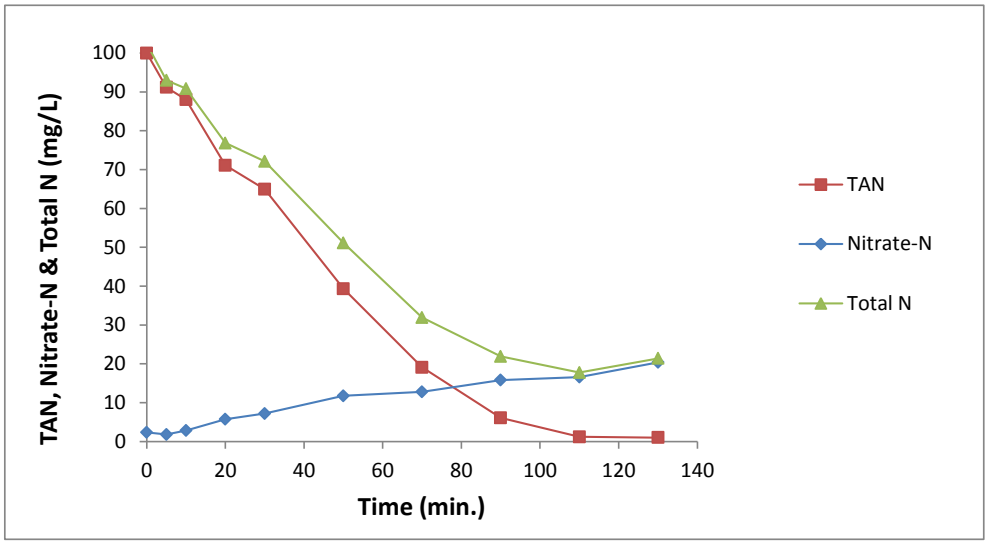


Figure 5.20: TAN removal, nitrate N and Total N in sample with initial 100 mg TAN/L, 20,000 mg NaCl/L at 3.0 A current

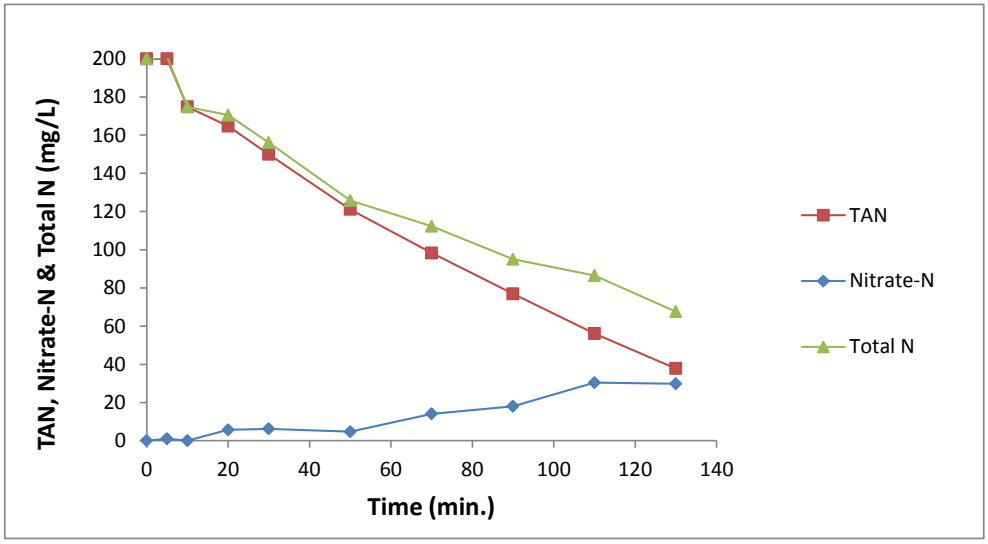


Figure 5.21: TAN removal, nitrate N and Total N in sample with initial 200 mg TAN/L, 20,000 mg NaCl/L, at 3.0 A current

In order to calculate energy requirements for present study, the method adopted was based on the specific electrical charge required to remove ammonia from the sample, expressed as:

$Q = \frac{J \times A \times t}{V}$

where, Q = specific charge, Ah/L

J = current density, A/cm^2

A = electrode surface area, cm^2

t = time, h

V = reactor volume, L

[Source: Anglada et al.(2009) [56], Kapalka et al. (2010) [73]]

Fig.5.22 shows the specific charge required for TAN removal at varying current and constant NaCl concentration of 10,000 mg/L. Fig.5.23 shows the specific charge required for TAN removal at varying NaCl concentration and a constant current of 3.0 A.

These two plots were selected since these were the optimum values established from the first set of experiments (Section 5.1)for each parameter. Fig.5.22 shows that at 10,000 mg NaCl/L, the effect of current variation on TAN removal is not significant. TAN content of all samples (with initial TAN 40 mg/L) is approximately 16 mg/L (60% removal) after a specific charge of 1.5 Ah/L. The test with 0.5 A current does not reach specific charge 1.5 Ah/L even after 130 minutes of treatment, but it is clear from the plot that for all samples the TAN removal characteristics for a particular specific charge is almost the same.

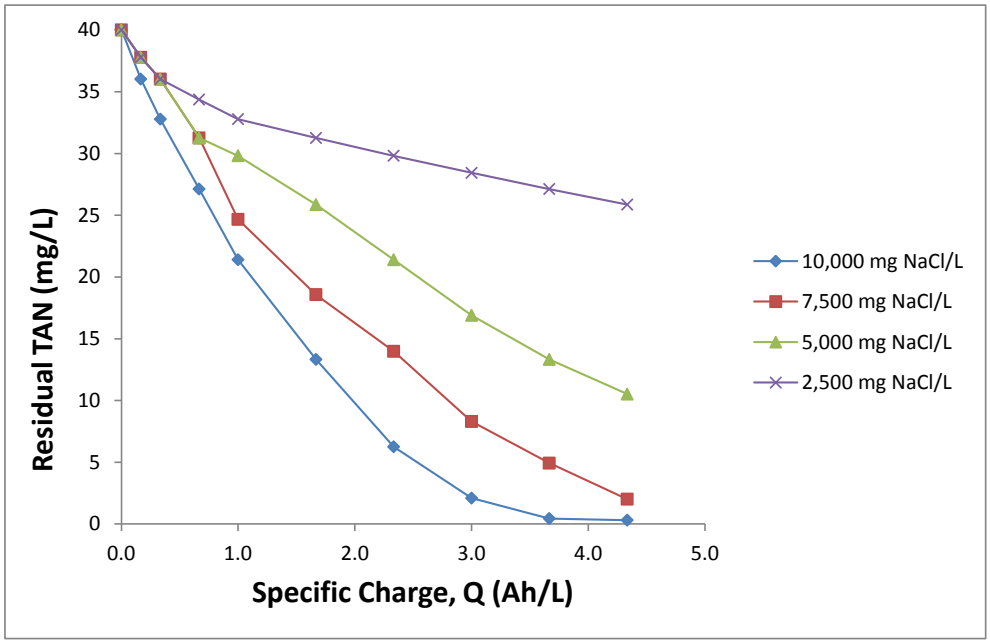


Figure 5.22: Specific charge required for ammonia removal at various NaCl concentration

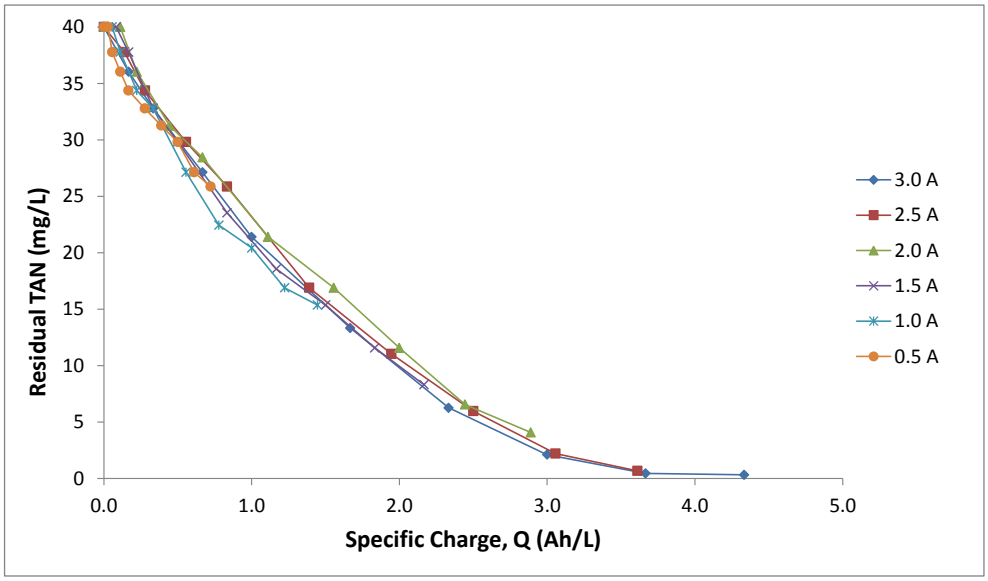


Figure 5.23: Specific charge required for ammonia removal at various current

Thus it can be concluded that specific charge for TAN removal is not dependent on applied current. However, from Fig.5.23 it can be noticed that variation of NaCl concentration has a significant effect on TAN removal. A specific charge of 4.33 Ah/L only reduced TAN from an initial 40 mg/L to 22.44 mg/L (44% removal) for 2,500 mg NaCl/L, whereas the same specific charge reduced the TAN to 0.32 mg/L (99% removal) for sample with 10,000 mg NaCl/L. Higher NaCl concentrations, therefore, are very much favorable for minimizing the specific charge requirements for TAN removal. This is again related to the evolution of chlorine gas and HOCl acid. The rate of chlorine gas formation at the anode is much quicker for samples with higher NaCl concentrations owing to the abundance of chloride ions. Therefore, the specific charge required to form a certain amount of HOCl from sample with high NaCl content is much lower compared to samples with lower NaCl content. This is also a re-iteration of the previous inference (from Sections 5.3 and 5.4) that the rate limiting factor of TAN removal process is the evolution of chlorine gas at the anode.

The same conclusions apply for higher concentrations of sodium chloride, results of which were plotted in Fig.5.24. Sample with lowest NaCl concentration (10,000 mg/L) showed only 32.2% TAN removal after treatment with 0.67 Ah/L, whereas higher NaCl concentrations of 20,000, 30,000 and 50,000 mg/L exhibited 49.0%, 90.9% and 98.4% TAN removal respectively. Higher chloride content is shown to remove TAN at the expense of much lower energy requirements.

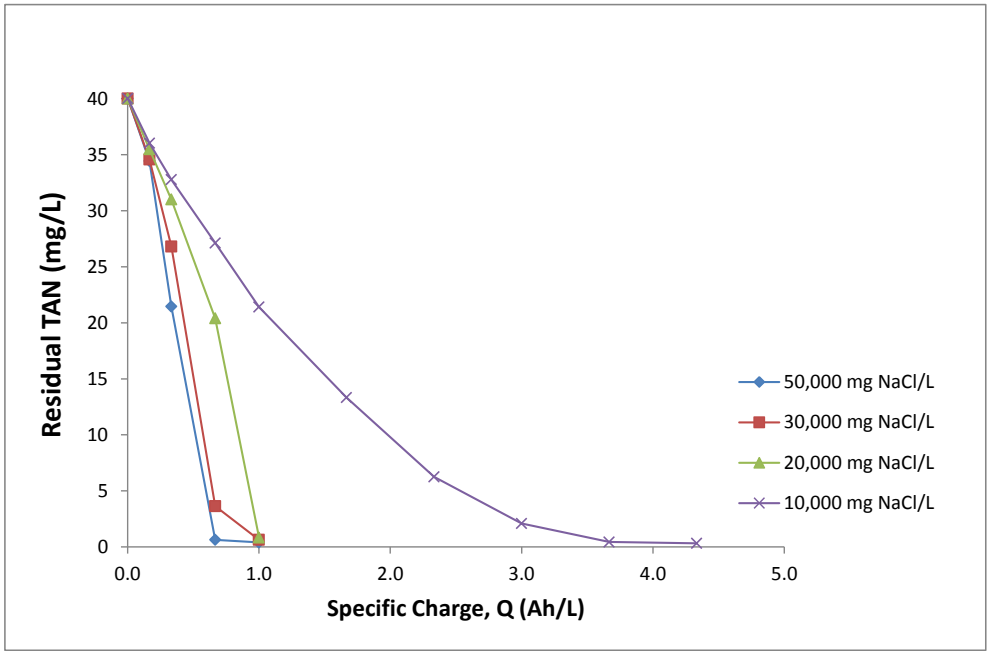


Figure 5.24: Specific charge required for ammonia removal at higher NaCl concentration

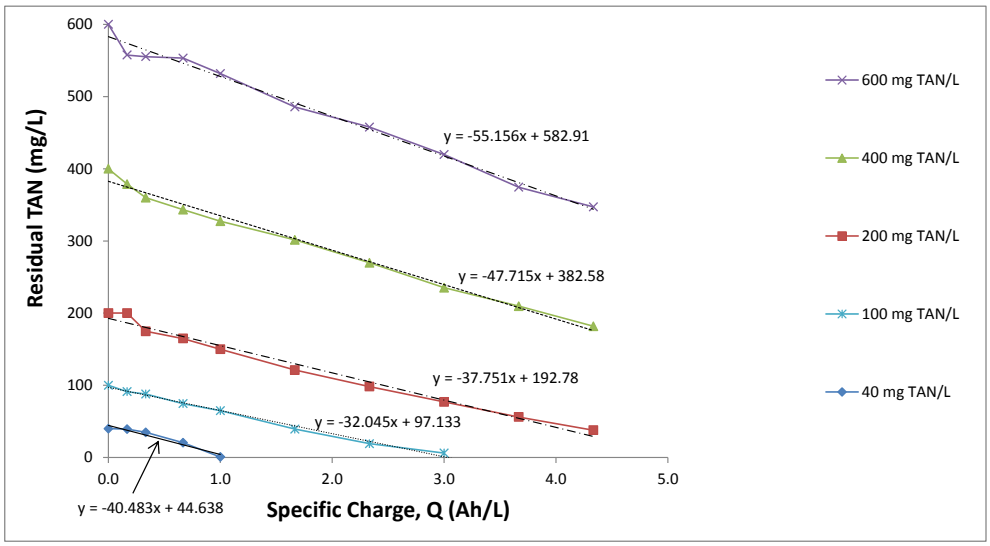


Figure 5.25: Specific charge required for ammonia removal at various TAN concentration

Fig.5.25 shows the specific charge required for TAN removal at different initial TAN values. This plot is similar to Fig.5.17 because in this case TAN removal is plotted against specific charge, which is a function of time, whereas in Fig.5.17, the TAN removal is plotted against time. However, the plot in Fig.5.25 is necessary to determine specific charge requirements. It is noticeable that higher initial TAN concentrations require more specific charge. Samples with 40 and 100 mg/L initial TAN shows complete TAN removal after specific charge of 1.0 and 3.0 Ah/L respectively. However, samples with higher initial TAN of 200, 400 and 600 mg/L do not reach complete TAN removal even after 4.3 Ah/L of treatment (at the end of 130 minutes). This is because higher TAN concentrations require longer treatment time due to the greater amount of ammonia to be degraded. From the definition of specific charge, it follows that longer the treatment time, more the specific charge consumed.

Linear trend is followed by all samples in this plot, and the equation for each line has been displayed. Using these equations, it is possible to estimate the specific charge requirements that ensure each sample conforms to discharge standards. Considering that effluents should contain no more than 1 mg/L TAN, the samples with initial TAN concentrations 200, 400 and 600 mg/L would require 5.1, 8.0 and 10.6 Ah/L specific charge respectively.

Another parameter used to calculate energy demand of a process is power consumption, expressed as kWh/m^3. This is easily obtained from the calculated specific charge values by multiplying with the potential difference (voltage) applied

between the electrodes in order to pass electric current. Therefore the results obtained for power consumption during present study have very similar trends to those observed for specific charge. Nevertheless, it should be stated that higher NaCl concentration requires less power for the same current compared to samples with low NaCl concentration. This is due to the higher potential that needs to be maintained in order to apply the same current for low NaCl concentrations. Decrease in NaCl concentration decreases conductivity of the electrolyte, which makes it necessary to apply higher potential to achieve the same current.

5.7 Comparison of results with reports in literature

Table 5.1 makes a comparison between the results obtained in present study and those reported for other anode materials. The results reported in literature for ammonia removal using other anodes at different conditions are compared with the results obtained in the present study at similar conditions. This was done in order to evaluate the performance of graphite compared to other anode materials for ammonia removal from wastewater. The values pertaining to present study have been italicized in the table.

The term current density is used more commonly in literature in place of applied current. Current density is defined as the current applied per unit effective surface area of electrode. The current densities used in present study are 2.6, 5.2,

7.7, 10.3, 12.9 and 15.5 mA/cm^2 corresponding to applied currents of 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 A respectively. The chloride concentrations for samples with initial sodium chloride concentrations of 2,500, 5,000, 7,500 and 10,000 mg/L can be calculated as 1,515, 3,030 , 4,545 and 6,061 mg/L respectively.

The first parameter compared was specific charge, expressed as Ah/L. Kapalka et al. (2010) [74], using Ni/Ni(OH)$_2$ anodes, required 26.35 Ah/L of specific charge to achieve 55% TAN removal from sample with initial TAN 650 mg/L at a current density 20 mA/cm^2 and Cl^- content 37,278 mg/L after a treatment time of 12 h. Present study required much lesser specific charge of 10.56 Ah/L (less than half) to achieve 100% TAN removal from a sample with similar initial TAN of 600 mg/L, at a current density of 15.4 mA/cm^2 and much lower Cl^- content of 12,121 mg/L (one third) within a significantly shorter treatment time of 5.3 h (less than half). Thus, the superior performance of graphite over nickel electrodes for ammonia removal is established.

Kapalka et al. (2010) [73] used Boron-Doped Diamond (BDD) anode to achieve 100% TAN removal from an initial concentration of 650 mg/L and initial Cl^- content 5,800 mg/L using current density 30 mA/cm^2 within 2.4 h of treatment. The specific charge required for the process was 7.0 Ah/L. Present study required 10.56 Ah/L (1.5 times) for complete TAN removal from an initial TAN concentration of 650 mg/L (similar), but higher Cl^- content of 12,121 mg/L (roughly double) and current density 15.4 mA/cm^2 (half) after 5.3 h of treatment (2.2 times).

Table 5.1: Comparison of results with those reported in literature for other anodes

Sl. No.	**Anode**	**Comparison**			**Other parameters**							**Reference**
		Parameter	**Unit**	**Value**	**Initial TAN (mg/L)**	**TAN removed (mg/L)**	**TAN removal (%)**	**Cl^- (mg/L)**	**CD (mA/cm^2)**	**Treat -ment time (h)**	**pH**	
1	$Ni/Ni(OH)_2$	Specific charge	Ah/L	**26.35**	650	358	55	37,278	20.0	12.0	11.0	[74]
	Present study			***10.56***	*600*	*600*	*100*	*12,121*	*15.4*	*5.3*	*7.0*	
2	BDD			**7.00**	650	650	100	5,800	30.0	2.4	5.5	[73]
	Present study			***10.56***	*600*	*600*	*100*	*12,121*	*15.4*	*5.3*	*7.0*	
3	Ti/PtO_x-IrO_2			**7.70**	910	910	100	5,800	20.0	3.1	6.0	[59]
	Present study			***10.56***	*600*	*600*	*100*	*12,121*	*15.4*	*5.3*	*7.0*	
4	Ti/Pt-Ir			**22.00**	292	277	94.9	5,500	20.0	5.5	7.0	[67]
	Ti/PdO-Co_3O_4			**30.67**	358	343	95.8	5,500	20.0	7.7	7.0	
	Ti/RhO_x-TiO_2			**90.20**	257	242	94.2	5,500	20.0	22.6	7.0	
	Present study			***7.90***	*400*	*400*	*100*	*12,121*	*15.4*	*4.0*	*7.0*	
5	Ti/Pt	Power consu -mption	kWh/m^3	**90.00**	150	100	66.7	4,848	130.6	6.0	7.0	[72]
	Present study			***44.88***	*200*	*200*	*100*	*12,121*	*15.4*	*2.6*	*7.0*	
6	Ti/Pt			**201.60**	44	29	65.9	12,121	-	6.0	7.0	[76]
	Present study			***7.40***	*40*	*39*	*97.9*	*12,121*	*15.4*	*0.5*	*7.0*	
7	BDD			**0.78**	8	8	100	26,167	5.0	0.8	7.0	[75]
	Present study			***5.50***	*40*	*39.56*	*98.9*	*30,303*	*15.4*	*0.5*	*7.0*	

From this comparison, though BDD anodes show better performance, the results obtained using graphite are comparable.

Kapalka et al. (2010) [59] also used Ti/PtO_x-IrO_2 anode to remove TAN completely from a sample with initial TAN 910 mg/L and Cl^- 5,800 mg/L using 7.7 Ah/L specific charge after 3.1 h of treatment with a current density of 20 mA/cm^2. Present study required higher specific charge of 10.56 Ah/L (1.5 times) for complete TAN removal from an initial TAN concentration of 650 mg/L (0.71 times), but higher Cl^- content of 12,121 mg/L (roughly double) and current density 15.4 mA/cm^2 (0.75 times) after 5.3 h of treatment (1.5 times). This comparison shows that Ti/PtO_x-IrO_2 anode requires less energy for TAN removal compared to graphite.

Szpyrkowicz et al. (2005) [67] investigated three different anode materials for TAN removal. Out of those, Ti/Pt-Ir showed best performance, consuming 22.0 Ah/L specific charge to remove 94.9% TAN from an initial TAN concentration of 292 mg/L and Cl^- content 5,500 mg/L using 20 mA/cm^2 current density and 5.5 h treatment time. Other parameters such as COD, Cr and sulfides were also treated besides TAN. Present study required much lower specific charge of 7.9 Ah/L (roughly one-third) to achieve complete TAN removal from a sample containing 400 mg/L initial TAN (1.4 times higher) and Cl^- content of 12,121 mg/L (twice) at a current density 15.4 mA/cm^2 (0.75 times) after a treatment time of 4 h (0.73 times).

The other parameter compared was power consumption, in terms of kWh/m^3.

Though this is similar to specific charge, some of the reported works in literature calculated power consumption rather than specific charge. Vlyssides et al. (2002) [72] used Ti/Pt anode and 90.0 kWh/m^3 power to achieve 66.7% TAN removal from a sample with 150 mg/L initial TAN and 4,848 mg/L Cl^- content after 6 h treatment at a current density of 130.6 mA/cm^2. Parameters such as COD, VSS, nitrates and phosphorus were also treated. Present study needed only 44.9 kWh/m^3 power (half) to remove TAN completely from a sample with initial TAN 200 mg/L (1.3 times) and Cl^- content 12,121 mg/L (2.5 times) at a current density of 15.4 mA/cm^2 (less than 8 times) within 2.6 h of treatment (0.43 times). Though the chloride content was higher for present study, all other parameters are better, especially current density which is more than eight times lower.

Zorpas (2011) [76] also used Ti/Pt anode, reporting a power consumption of 201.6 kWh/m^3 to remove 65.9% TAN from a sample with initial TAN 44 mg/L and Cl^- content 12,121 mg/L after 6 h of treatment. COD, BOD and color were the other pollutants treated. Present study required only 7.4 kWh/m^3 (27 times lower) for complete TAN removal from sample with initial TAN 40 mg/l (similar) and Cl^- 12,121 mg/L (same) after just 0.5 h treatment (12 times shorter).

Diaz et al. (2011) [75] used BDD anode, requiring 0.78 kwh/m^3 to achieve complete TAN removal from an initial sample with 8 mg/L initial TAN and Cl^- content 26,167 mg/L at a current density of 5 mA/cm^2 after 0.8 h treatment. Nitrite and COD were the other parameters treated during the study. Present study required 5.5 kWh/m^3 (7 times higher) for complete TAN removal from

sample with initial TAN 40 mg/L (5 times) and Cl^- 30,303 mg/L (similar) at a current density of 15.4 mA/cm^2 (thrice) after 0.5 h treatment (0.6 times).

It was observed that the results obtained for ammonia removal from wastewater using graphite electrodes were comparable, if not better than those achieved using much more expensive materials such as titanium, platinum and boron-doped diamond. The only limitation found was that the wastewater requires high chloride content, which also applies for almost all anodes reported in literature. However, this can easily be achieved by the addition of sodium chloride which is cheap and available in abundance. Furthermore, the expensive materials used for ammonia removal by electro-oxidation have shown good results during lab-scale experiments, but the use of much bigger and expensive electrodes for a full-scale treatment plant seems highly uneconomical. Many of the electrodes reported in literature require preparation such as deposition of other materials on a substrate, while on the other hand graphite electrodes are much cheaper and easier to produce.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The following conclusions were made from this study:

(1) The TAN removal is found to be dependent on the applied current and chloride content of the sample. The higher the values of these two parameters, the more efficient is the removal.

(2) The dependency on chloride also establishes that the mechanism involved in these experiments is the indirect oxidation which proceeds by the formation of hypochlorous acid, a very strong oxidizing agent.

(3) TAN removal of $> 90\%$ was achieved for samples containing 4,500-6,000 mg/L chlorides within 130 minutes at a current of 3.0 A (15.5 mA/cm^2).

(4) For samples containing 18,000 mg/L chlorides, similar removal efficiency was achieved within 20 minutes using the same current.

(5) TAN concentration (40-600 mg/L) were used and it was found that at higher TAN values the treatment was effective, however longer treatment time is required.

(6) pH does not have a significant effect on TAN removal. At pH 1, TAN removal was greatly enhanced due to the high chloride content of the sample caused during the pH adjustment stage by the addition of large volume ($>$ 100 ml) of concentrated HCl.

(7) The pH value of all treated effluent is observed to be approximately 3, which may necessitate pH adjustment before discharge.

(8) It was observed that if the experiment is continued after TAN removal is nearly complete, the pH gradually increases. This phenomenon, not mentioned in literature, could be linked with the relative increase in NaOH concentration after the HCl formation ceases along with TAN degradation reaction.

(9) Nitrate was detected in the treated effluent and this is from a side-reaction during ammonia oxidation by HOCl. The rate of nitrate release was 0.18-0.21 mg/mg TAN removed, which would imply that the effluent conforms to the general discharge standards of 50 mg nitrate-N/L for waters with a TAN content up to 250 mg/L. This would make it suitable for the treatment of typical municipal wastewater.

(10) The graphite electrodes require highly saline waters for effective treatment. Electrode fouling was observed below 3,000 mg/L chloride concentrations, signifying that these electrodes require high conductivity of electrolyte.

(11) Energy consumption for TAN removal by graphite electrodes was found to be nearly three times lower than Ti/Pt-Ir electrodes. However, Boron-Doped Diamond (BDD) electrodes showed lower power consumption compared to graphite.

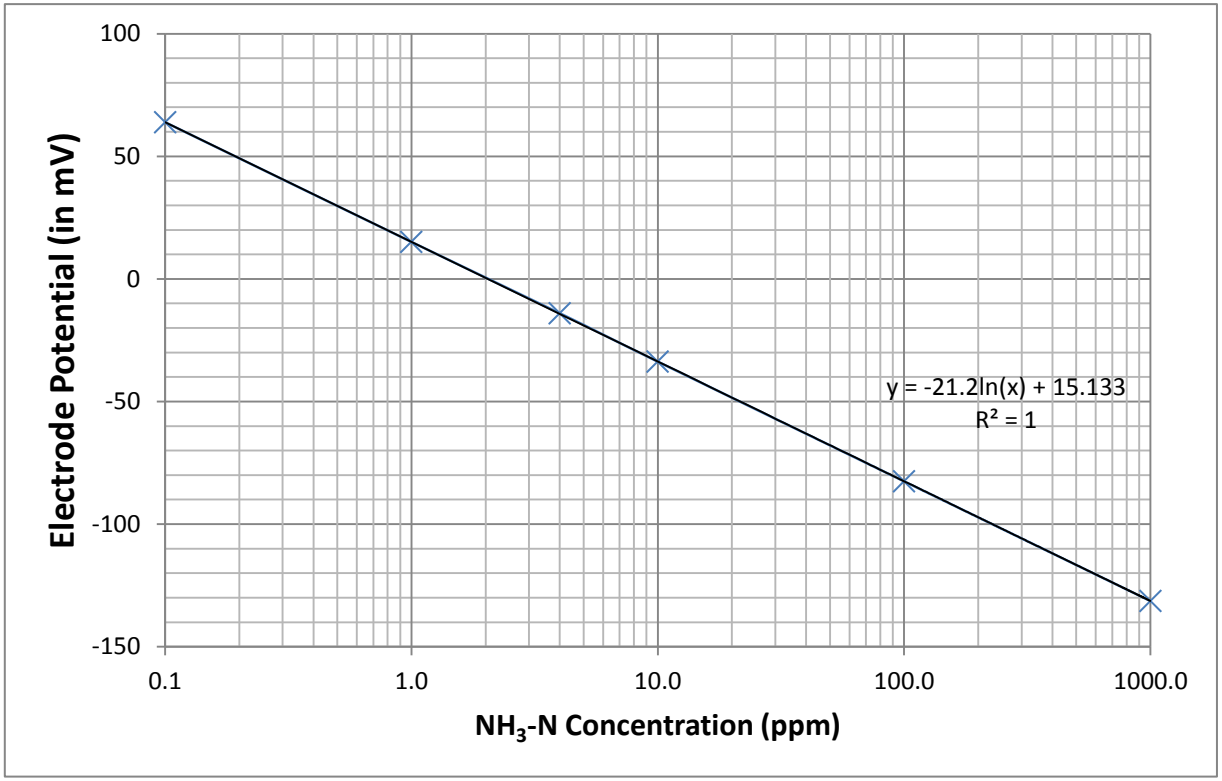
6.2 Recommendations

(1) The use of graphite electrodes for ammonia removal might be a feasible option for wastewaters having high chloride content and TAN values upto 250 mg/L, assuming 50 mg/L as the discharge standard for nitrate. Higher TAN concentrations can also be treated but with polishing of effluent before discharge.

(2) Further research is needed to evaluate the economic feasibility of such a treatment facility.

APPENDIX

APPENDIX - A 1 CALIBRATION CURVE FOR AMMONIA ION-SELECTIVE ELECTRODE (ISE)
- FIRST SET OF EXPERIMENTS (DETERMINATION OF OPTIMUM PARAMETERS)



NH_3-N Concentration (ppm)	Electrode Potential (mV)
0.1	64
1.0	15
4.0	-14
10.0	-34
100.0	-83
1000.0	-131

APPENDIX - A 2 **AMMONIA REMOVAL FOR VARYING NaCl CONCENTRATIONS AT A CONSTANT CURRENT OF 0.5 A, UNADJUSTED pH**

NaCl concentration (mg/L)	Time (min)	pH	ISE Reading (mV)	Corresponding ppm	x (Dilution Factor)	Ammonia removal (%)
2,500	**Applied Potential = 5.5 V**					
	0	6.72	-14	4.00	40.00	0.00
	5	6.21	-14	4.00	40.00	0.00
	10	5.86	-14	4.00	40.00	0.00
	20	4.94	-14	4.00	40.00	0.00
	30	4.52	-14	4.00	40.00	0.00
	50	3.98	-14	4.00	40.00	0.00
	70	3.84	-14	4.00	40.00	0.00
	90	3.64	-14	4.00	40.00	0.00
	110	3.48	-14	4.00	40.00	0.00
	130	3.45	-14	4.00	40.00	0.00
5,000	**Applied Potential = 5.2 V**					
	0	6.80	-14	4.00	40.00	0.00
	5	6.02	-14	4.00	40.00	0.00
	10	5.71	-14	4.00	40.00	0.00
	20	4.87	-13	3.78	37.78	5.56
	30	4.32	-13	3.78	37.78	5.56
	50	3.85	-12	3.60	36.03	9.93
	70	3.71	-11	3.44	34.36	14.09
	90	3.57	-11	3.44	34.36	14.09
	110	3.44	-10	3.28	32.77	18.07
	130	3.41	-10	3.28	32.77	18.07
7,500	**Applied Potential = 5.1 V**					
	0	6.09	-14	4.00	40.00	0.00
	5	5.87	-14	4.00	40.00	0.00
	10	5.77	-14	4.00	40.00	0.00
	20	5.04	-13	3.78	37.78	5.56
	30	4.25	-12	3.60	36.03	9.93
	50	3.81	-11	3.44	34.36	14.09
	70	3.65	-10	3.28	32.77	18.07
	90	3.45	-9	3.13	31.26	21.86
	110	3.36	-8	2.98	29.81	25.47
	130	3.24	-7	2.84	28.43	28.92
10,000	**Applied Potential = 4.7 V**					
	0	6.11	-14	4.00	40.00	0.00
	5	4.42	-14	4.00	40.00	0.00
	10	4.31	-13	3.78	37.78	5.56
	20	4.17	-12	3.60	36.03	9.93
	30	4.04	-11	3.44	34.36	14.09
	50	3.66	-10	3.28	32.77	18.07
	70	3.38	-9	3.13	31.26	21.86
	90	3.29	-8	2.98	29.81	25.47
	110	3.15	-6	2.71	27.12	32.20
	130	3.11	-5	2.59	25.86	35.34

APPENDIX - A 3 **AMMONIA REMOVAL FOR VARYING NaCl CONCENTRATIONS AT A CONSTANT CURRENT OF 1.0 A, UNADJUSTED pH**

NaCl concentration (mg/L)	Time (min)	pH	ISE Reading (mV)	Corresponding ppm	x (Dilution Factor)	Ammonia removal (%)
2,500	**Applied Potential = 9.8 V**					
	0	6.42	-14	4.00	40.00	0.00
	5	6.23	-14	4.00	40.00	0.00
	10	5.96	-14	4.00	40.00	0.00
	20	5.66	-14	4.00	40.00	0.00
	30	5.28	-14	4.00	40.00	0.00
	50	4.85	-14	4.00	40.00	0.00
	70	4.13	-14	4.00	40.00	0.00
	90	3.97	-14	4.00	40.00	0.00
	110	3.68	-14	4.00	40.00	0.00
	130	3.61	-14	4.00	40.00	0.00
5,000	**Applied Potential = 8.4 V**					
	0	6.40	-14	4.00	40.00	0.00
	5	5.04	-14	4.00	40.00	0.00
	10	4.63	-14	4.00	40.00	0.00
	20	4.40	-13	3.78	37.78	5.56
	30	4.20	-12	3.60	36.03	9.93
	50	3.92	-11	3.44	34.36	14.09
	70	3.64	-9	3.13	31.26	21.86
	90	3.45	-8	2.98	29.81	25.47
	110	3.29	-6	2.71	27.12	32.20
	130	3.20	-5	2.59	25.86	35.34
7,500	**Applied Potential = 7.6 V**					
	0	5.87	-14	4.00	40.00	0.00
	5	4.03	-13	3.78	37.78	5.56
	10	3.84	-12	3.60	36.03	9.93
	20	3.72	-11	3.44	34.36	14.09
	30	3.68	-10	3.28	32.77	18.07
	50	3.30	-8	2.98	29.81	25.47
	70	3.13	-6	2.71	27.12	32.20
	90	3.06	-4	2.47	24.67	38.33
	110	2.96	-2	2.24	22.44	43.90
	130	2.85	-2	2.24	22.44	43.90
10,000	**Applied Potential = 6.5 V**					
	0	6.11	-14	4.00	40.00	0.00
	5	5.10	-14	4.00	40.00	0.00
	10	4.70	-13	3.78	37.78	5.56
	20	3.57	-11	3.44	34.36	14.09
	30	3.30	-10	3.28	32.77	18.07
	50	3.12	-6	2.71	27.12	32.20
	70	3.07	-2	2.24	22.44	43.90
	90	2.98	0	2.04	20.41	48.97
	110	2.92	4	1.69	16.89	57.77
	130	2.90	6	1.54	15.36	61.59

APPENDIX - A 4 **AMMONIA REMOVAL FOR VARYING NaCl CONCENTRATIONS AT A CONSTANT CURRENT OF 1.5 A, UNADJUSTED pH**

NaCl concentration (mg/L)	Time (min)	pH	ISE Reading (mV)	Corresponding ppm	x (Dilution Factor)	Ammonia removal (%)
2,500	**Applied Potential = 13.2 V**					
	0	6.45	-14	4.00	40.00	0.00
	5	6.30	-14	4.00	40.00	0.00
	10	5.71	-14	4.00	40.00	0.00
	20	4.68	-13	3.78	37.78	5.56
	30	3.79	-13	3.78	37.78	5.56
	50	3.40	-12	3.60	36.03	9.93
	70	3.26	-11	3.44	34.36	14.09
	90	3.10	-10	3.28	32.77	18.07
	110	3.05	-9	3.13	31.26	21.86
	130	3.01	-8	2.98	29.81	25.47
5,000	**Applied Potential = 9.9 V**					
	0	6.36	-14	4.00	40.00	0.00
	5	4.59	-14	4.00	40.00	0.00
	10	4.34	-13	3.78	37.78	5.56
	20	4.05	-12	3.60	36.03	9.93
	30	3.76	-11	3.44	34.36	14.09
	50	3.44	-9	3.13	31.26	21.86
	70	3.20	-7	2.84	28.43	28.92
	90	3.06	-6	2.71	27.12	32.20
	110	2.98	-4	2.47	24.67	38.33
	130	2.94	-2	2.24	22.44	43.90
7,500	**Applied Potential = 8.3 V**					
	0	5.96	-14	4.00	40.00	0.00
	5	5.31	-13	3.78	37.78	5.56
	10	4.61	-12	3.60	36.03	9.93
	20	3.81	-11	3.44	34.36	14.09
	30	3.50	-10	3.28	32.77	18.07
	50	3.23	-7	2.84	28.43	28.92
	70	3.08	-4	2.47	24.67	38.33
	90	3.01	-1	2.14	21.40	46.50
	110	2.95	1	1.95	19.47	51.33
	130	2.91	3	1.77	17.71	55.73
10,000	**Applied Potential = 7.9 V**					
	0	6.23	-14	4.00	40.00	0.00
	5	3.78	-14	4.00	40.00	0.00
	10	3.63	-13	3.78	37.78	5.56
	20	3.40	-10	3.28	32.77	18.07
	30	3.21	-8	2.98	29.81	25.47
	50	3.02	-3	2.35	23.53	41.18
	70	2.95	2	1.86	18.57	53.58
	90	2.88	6	1.54	15.36	61.59
	110	2.86	12	1.16	11.56	71.09
	130	2.86	19	0.83	8.30	79.24

APPENDIX - A 5 AMMONIA REMOVAL FOR VARYING NaCl CONCENTRATIONS AT A CONSTANT CURRENT OF 2.0 A, UNADJUSTED pH

NaCl concentration (mg/L)	Time (min)	pH	ISE Reading (mV)	Corresponding ppm	x (Dilution Factor)	Ammonia removal (%)
2,500	**Applied Potential = 14.1 V**					
	0	6.31	-14	4.00	40.00	0.00
	5	3.84	-14	4.00	40.00	0.00
	10	3.83	-14	4.00	40.00	0.00
	20	3.75	-13	3.78	37.78	5.56
	30	3.67	-12	3.60	36.03	9.93
	50	3.35	-11	3.44	34.36	14.09
	70	3.20	-10	3.28	32.77	18.07
	90	3.07	-9	3.13	31.26	21.86
	110	2.99	-8	2.98	29.81	25.47
	130	2.97	-7	2.84	28.43	28.92
5,000	**Applied Potential = 10.5 V**					
	0	6.31	-14	4.00	40.00	0.00
	5	3.84	-13	3.78	37.78	5.56
	10	3.83	-13	3.78	37.78	5.56
	20	3.75	-11	3.44	34.36	14.09
	30	3.67	-10	3.28	32.77	18.07
	50	3.35	-8	2.98	29.81	25.47
	70	3.20	-6	2.71	27.12	32.20
	90	3.07	-3	2.35	23.53	41.18
	110	2.99	-1	2.14	21.40	46.50
	130	2.97	1	1.95	19.47	51.33
7,500	**Applied Potential = 9.9 V**					
	0	5.95	-14	4.00	40.00	0.00
	5	4.31	-13	3.78	37.78	5.56
	10	3.96	-13	3.78	37.78	5.56
	20	3.54	-11	3.44	34.36	14.09
	30	3.31	-9	3.13	31.26	21.86
	50	3.10	-6	2.71	27.12	32.20
	70	2.99	-2	2.24	22.44	43.90
	90	2.89	2	1.86	18.57	53.58
	110	2.88	6	1.54	15.36	61.59
	130	2.87	10	1.27	12.71	68.22
10,000	**Applied Potential = 8.3 V**					
	0	6.24	-14	4.00	40.00	0.00
	5	6.11	-14	4.00	40.00	0.00
	10	5.40	-12	3.60	36.03	9.93
	20	3.67	-9	3.13	31.26	21.86
	30	3.32	-7	2.84	28.43	28.92
	50	3.08	-1	2.14	21.40	46.50
	70	3.02	4	1.69	16.89	57.77
	90	2.93	12	1.16	11.56	71.09
	110	2.92	24	0.66	6.55	83.62
	130	2.91	34	0.41	4.08	89.80

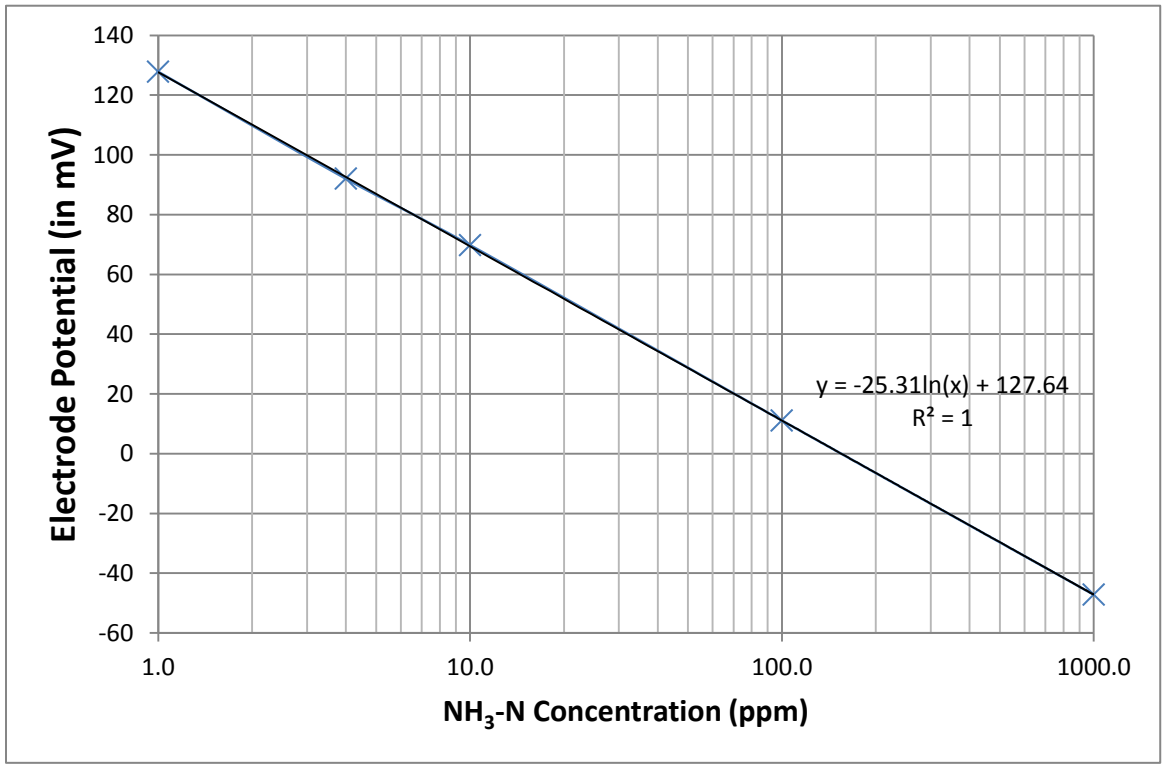
APPENDIX - A 6 AMMONIA REMOVAL FOR VARYING NaCl CONCENTRATIONS AT A CONSTANT CURRENT OF 2.5 A, UNADJUSTED pH

NaCl concentration (mg/L)	Time (min)	pH	ISE Reading (mV)	Corresponding ppm	x (Dilution Factor)	Ammonia removal
2,500	**Applied Potential = 18.0 V**					
	0	6.53	-14	4.00	40.00	0.00
	5	4.52	-14	4.00	40.00	0.00
	10	4.36	-13	3.78	37.78	5.56
	20	4.23	-12	3.60	36.03	9.93
	30	3.98	-11	3.44	34.36	14.09
	50	3.57	-10	3.28	32.77	18.07
	70	3.41	-9	3.13	31.26	21.86
	90	3.32	-8	2.98	29.81	25.47
	110	3.18	-7	2.84	28.43	28.92
	130	3.06	-6	2.71	27.12	32.20
5,000	**Applied Potential = 12.3 V**					
	0	6.32	-14	4.00	40.00	0.00
	5	5.56	-13	3.78	37.78	5.56
	10	5.39	-12	3.60	36.03	9.93
	20	4.61	-10	3.28	32.77	18.07
	30	4.01	-9	3.13	31.26	21.86
	50	3.50	-7	2.84	28.43	28.92
	70	3.31	-4	2.47	24.67	38.33
	90	3.19	-1	2.14	21.40	46.50
	110	3.07	2	1.86	18.57	53.58
	130	3.00	6	1.54	15.36	61.59
7,500	**Applied Potential = 10.3 V**					
	0	5.90	-14	4.00	40.00	0.00
	5	4.96	-13	3.78	37.78	5.56
	10	4.93	-12	3.60	36.03	9.93
	20	4.14	-10	3.28	32.77	18.07
	30	3.43	-7	2.84	28.43	28.92
	50	3.19	-2	2.24	22.44	43.90
	70	3.07	3	1.77	17.71	55.73
	90	2.97	10	1.27	12.71	68.22
	110	2.82	20	0.79	7.92	80.20
	130	2.87	30	0.49	4.93	87.67
10,000	**Applied Potential = 8.8 V**					
	0	5.85	-14	4.00	40.00	0.00
	5	5.30	-13	3.78	37.78	5.56
	10	4.32	-11	3.44	34.36	14.09
	20	3.53	-8	2.98	29.81	25.47
	30	3.27	-5	2.59	25.86	35.34
	50	3.10	4	1.69	16.89	57.77
	70	2.99	13	1.10	11.03	72.43
	90	2.95	26	0.60	5.96	85.10
	110	2.93	47	0.22	2.21	94.49
	130	2.90	72	0.07	0.68	98.31

APPENDIX - A 7 AMMONIA REMOVAL FOR VARYING NaCl CONCENTRATIONS AT A CONSTANT CURRENT OF 3.0 A, UNADJUSTED pH

NaCl concentration (mg/L)	Time (min)	pH	ISE Reading (mV)	Corresponding ppm	x (Dilution Factor)	Ammonia removal (%)
2,500	**Applied Potential = 18.3 V**					
	0	6.26	-14	4.00	40.00	0.00
	5	5.95	-13	3.78	37.78	0.00
	10	5.38	-12	3.60	36.03	9.93
	20	5.01	-11	3.44	34.36	14.09
	30	4.46	-10	3.28	32.77	18.07
	50	3.81	-9	3.13	31.26	21.86
	70	3.54	-8	2.98	29.81	25.47
	90	3.33	-7	2.84	28.43	28.92
	110	3.10	-6	2.71	27.12	32.20
	130	3.00	-5	2.59	25.86	35.34
5,000	**Applied Potential = 13.5 V**					
	0	6.29	-14	4.00	40.00	0.00
	5	5.95	-14	3.96	39.61	0.00
	10	5.47	-11	3.44	34.36	14.09
	20	4.90	-9	3.13	31.26	21.86
	30	3.78	-8	2.98	29.81	25.47
	50	3.30	-5	2.59	25.86	35.34
	70	3.12	-1	2.14	21.40	46.50
	90	2.98	4	1.69	16.89	57.77
	110	2.88	9	1.33	13.33	66.68
	130	2.85	14	1.05	10.52	73.70
7,500	**Applied Potential = 10.7 V**					
	0	6.21	-14	4.00	40.00	0.00
	5	5.80	-13	3.78	37.78	5.56
	10	5.00	-12	3.60	36.03	9.93
	20	3.93	-9	3.13	31.26	21.86
	30	3.47	-5	2.59	25.86	35.34
	50	3.10	2	1.86	18.57	53.58
	70	3.07	10	1.27	12.71	68.22
	90	3.01	19	0.83	8.30	79.24
	110	2.94	30	0.49	4.93	87.67
	130	2.92	49	0.20	2.01	94.99
10,000	**Applied Potential = 9.5 V**					
	0	6.22	-14	4.00	40.00	0.00
	5	5.21	-12	3.60	36.03	9.93
	10	4.09	-10	3.28	32.77	18.07
	20	3.51	-6	2.71	27.12	32.20
	30	3.26	-1	2.14	21.40	46.50
	50	3.00	9	1.33	13.33	66.68
	70	3.04	25	0.62	6.25	84.38
	90	3.03	48	0.21	2.10	94.74
	110	3.74	81	0.04	0.44	98.90
	130	4.59	88	0.03	0.32	99.21

APPENDIX - B 1 CALIBRATION CURVE FOR AMMONIA ION-SELECTIVE ELECTRODE (ISE) - SECOND SET OF EXPERIMENTS (EFFECT OF INITIAL pH)



NH_3-N Concentration (ppm)	Electrode Potential (mV)
1.0	127.8
4.0	92.0
10.0	69.8
100.0	11.1
1000.0	-47.2

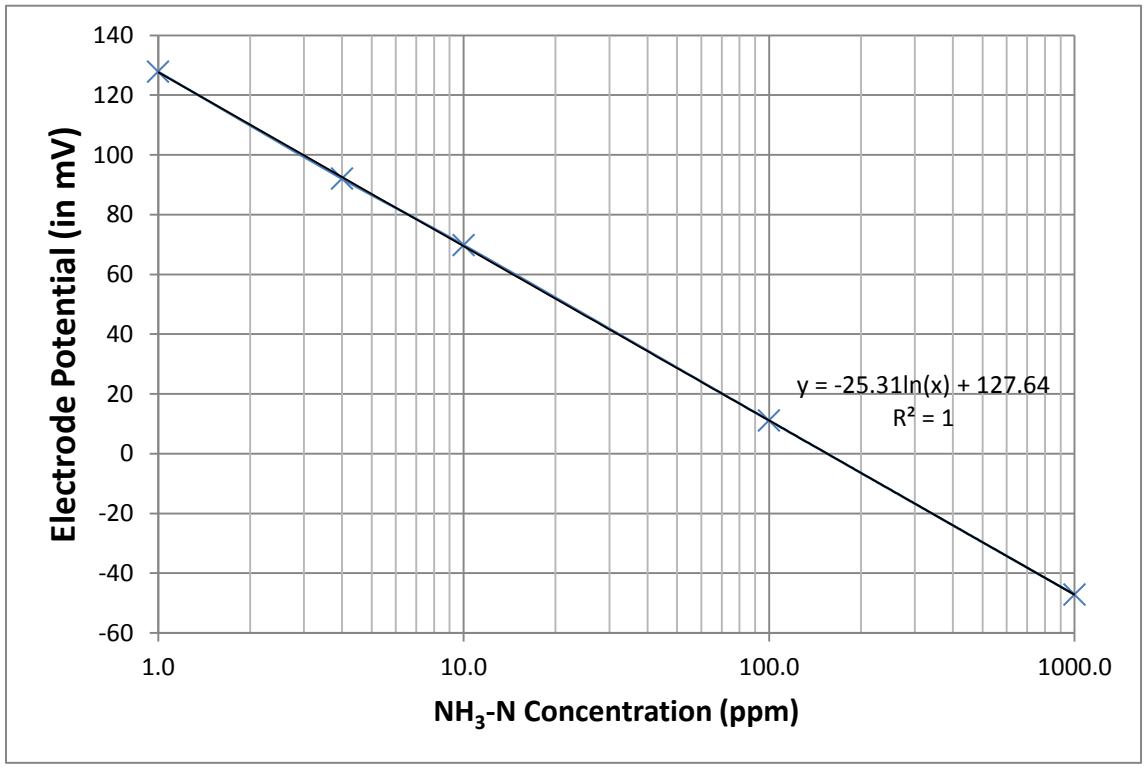
APPENDIX - B 2 (a) AMMONIA REMOVAL FOR VARYING INITIAL pH AT A CONSTANT CURRENT OF 3.0 A, NaCl CONCENTRATION 10,000 mg/L

Initial pH	Time (min)	pH	ISE Reading (mV)	Corresponding ppm	x (Dilution Factor)	Ammonia removal (%)
1	**Applied Potential = 6.2 V**					
	0	1.00	92.8	4.00	40.00	0.00
	5	1.01	98.6	3.18	31.80	20.49
	10	1.01	106.5	2.33	23.29	41.78
	20	0.98	119.1	1.42	14.17	64.58
	30	0.98	134.9	0.76	7.60	81.01
	50	1.06	174.6	0.16	1.59	96.03
	70	1.04	174.6	0.16	1.59	96.03
	90	-	-	-	-	-
	110	-	-	-	-	-
	130	-	-	-	-	-
2	**Applied Potential = 9.4 V**					
	0	2.00	91.6	4.00	40.00	0.00
	5	1.97	96.3	3.48	34.82	12.94
	10	1.99	98.1	3.24	32.44	18.91
	20	1.99	102.7	2.71	27.05	32.36
	30	1.99	107.6	2.23	22.30	44.25
	50	2.02	122.8	1.22	12.24	69.39
	70	2.01	137.6	0.68	6.83	82.93
	90	1.96	174.4	0.16	1.60	96.00
	110	-	-	-	-	-
	130	-	-	-	-	-
3	**Applied Potential = 10.2 V**					
	0	3.00	92.8	4.00	40.00	0.00
	5	2.79	95.0	3.67	36.66	8.36
	10	2.77	99.4	3.08	30.82	22.96
	20	2.74	102.7	2.71	27.05	32.36
	30	2.72	107.2	2.27	22.65	43.36
	50	2.58	125.9	1.08	10.83	72.92
	70	2.62	143.4	0.54	5.43	86.42
	90	2.75	159.5	0.29	2.88	92.80
	110	3.09	157.2	0.32	3.15	92.12
	130	3.54	178.4	0.14	1.37	96.59
4	**Applied Potential = 10.4 V**					
	0	4.00	96.5	4.00	40.00	0.00
	5	3.28	99.7	3.05	30.45	23.87
	10	3.19	101.7	2.81	28.14	29.64
	20	3.08	106.7	2.31	23.11	42.24
	30	3.04	112.5	1.84	18.38	54.05
	50	2.97	128.1	0.99	9.93	75.17
	70	2.91	147.0	0.47	4.71	88.22
	90	3.03	181.3	0.12	1.22	96.95
	110	3.58	190.6	0.08	0.84	97.89
	130	-	-	-	-	-

APPENDIX - B 2 (b) AMMONIA REMOVAL FOR VARYING INITIAL pH AT A CONSTANT CURRENT OF 3.0 A, NaCl CONCENTRATION 10,000 mg/L

Initial pH	Time (min)	pH	ISE Reading (mV)	Corresponding ppm	x (Dilution Factor)	Ammonia removal (%)
5	**Applied Potential = 9.4 V**					
	0	5.00	92.2	4.00	40.00	0.00
	5	3.23	98.2	3.23	32.31	19.23
	10	3.16	100.1	3.00	29.98	25.06
	20	3.09	105.6	2.41	24.13	39.68
	30	3.01	111.2	1.93	19.35	51.63
	50	2.92	125.9	1.08	10.83	72.92
	70	2.92	146.1	0.49	4.88	87.79
	90	2.98	174.0	0.16	1.62	95.94
	110	3.54	184	0.11	1.09499607	96.30
	130	5.07	194	0.07	0.73806267	96.90
6.8	**Applied Potential = 10.0 V**					
	0	6.80	92.8	4.00	40.00	0.00
	5	2.98	98.0	3.26	32.57	18.59
	10	2.96	100.3	2.97	29.74	25.65
	20	2.87	102.9	2.68	26.84	32.90
	30	2.79	105.5	2.42	24.23	39.44
	50	2.66	123.0	1.21	12.15	69.63
	70	2.60	145.6	0.50	4.98	87.55
	90	2.71	152.9	0.37	3.73	90.66
	110	-	-	-	-	-
	130	-	-	-	-	-
9	**Applied Potential = 10.1 V**					
	0	9.04	94.1	4.00	40.00	0.00
	5	6.42	96.6	3.44	34.41	13.96
	10	5.59	98.7	3.17	31.68	20.80
	20	3.71	104.2	2.55	25.50	36.25
	30	3.45	111.5	1.91	19.12	52.20
	50	3.32	121.3	1.30	12.99	67.53
	70	3.28	147.3	0.47	4.66	88.36
	90	3.44	164.4	0.24	2.37	94.07
	110	4.54	181.8	0.12	1.19	97.01
	130	4.57	174.3	0.16	1.61	95.99

APPENDIX - C 1 CALIBRATION CURVE FOR AMMONIA ION-SELECTIVE ELECTRODE (ISE)
- THIRD SET OF EXPERIMENTS (VARYING INITIAL AMMONIA CONCENTRATION)



NH_3-N Concentration (ppm)	Electrode Potential (mV)
1.0	127.8
4.0	92.0
10.0	69.8
100.0	11.1
1000.0	-47.2

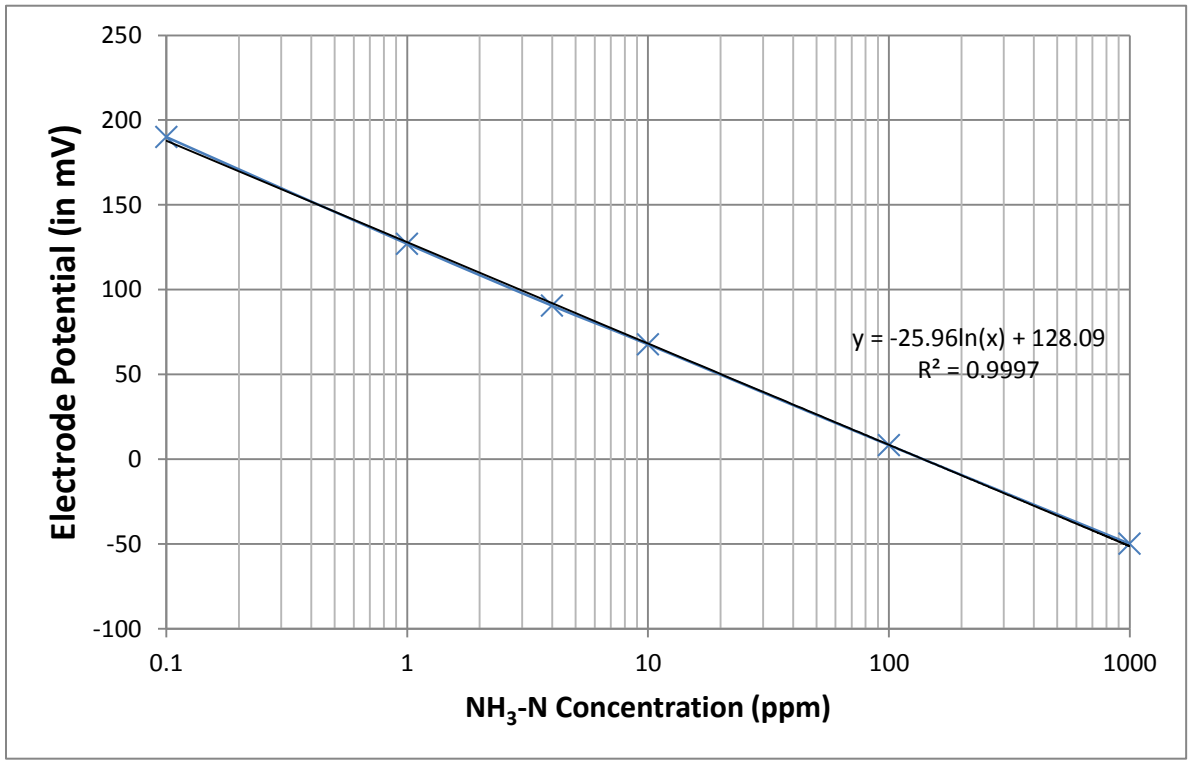
APPENDIX - C 2(a) AMMONIA REMOVAL FOR VARYING INITIAL AMMMONIA AT A CONSTANT CURRENT OF 3.0 A, NaCl CONCENTRATION 20,000 mg/L

Initial NH_3-N (ppm)	Time (min)	pH	ISE Reading (mV)	Corresponding ppm	x (Dilution Factor)	Ammonia removal (%)
	Applied Potential = 7.4 V					
	0	6.38	90.5	4.00	40.00	0.00
	5	3.19	92.4	3.94	39.41	1.48
	10	3.11	95.6	3.48	34.84	12.91
	20	3.03	109.5	2.04	20.39	49.02
40	30	3.05	192.2	0.08	0.84	97.89
	50	-	-	-	-	-
	70	-	-	-	-	-
	90	-	-	-	-	-
	110	-	-	-	-	-
	130	-	-	-	-	-
	Applied Potential = 6.8 V					
	0	5.20	68.5	10.00	100.00	0.00
	5	3.34	71.9	9.12	91.18	8.82
	10	3.14	72.8	8.80	88.00	12.00
	20	2.91	78.2	7.11	71.12	28.88
100	30	2.78	80.5	6.49	64.95	35.05
	50	2.63	93.2	3.94	39.35	60.65
	70	2.56	111.5	1.91	19.12	80.88
	90	2.55	140.4	0.61	6.11	93.89
	110	2.87	181.5	0.12	1.21	98.79
	130	3.75	185.7	0.10	1.02	98.98
	Applied Potential = 8.8 V					
	0	6.20	49.9	20.00	200.00	0.00
	5	3.56	51.7	20.00	200.00	0.00
	10	3.34	55.4	17.48	174.82	12.59
	20	3.03	56.9	16.48	164.77	17.61
200	30	2.83	59.3	14.99	149.89	25.06
	50	2.57	64.7	12.11	121.13	39.43
	70	2.50	70.0	9.83	98.28	50.86
	90	2.45	76.2	7.70	76.95	61.52
	110	2.42	84.2	5.61	56.13	71.94
	130	2.41	94.2	3.78	37.83	81.08
	Applied Potential = 7.9 V					
	0	6.78	35.6	40.00	400.00	0.00
	5	4.00	35.8	37.88	378.76	5.31
	10	3.49	37.1	35.98	359.83	10.04
	20	3.02	38.3	34.32	343.19	14.20
400	30	2.82	41.1	30.73	307.30	23.17
	50	2.56	41.6	30.13	301.30	24.67
	70	2.42	44.4	26.98	269.79	32.55
	90	2.25	49.7	21.89	218.89	45.28
	110	2.23	50.8	20.96	209.60	47.60
	130	2.18	54.4	18.18	181.85	54.54

APPENDIX - C 2 (b) AMMONIA REMOVAL FOR VARYING INITIAL AMMMONIA AT A CONSTANT CURRENT OF 3.0 A, NaCl CONCENTRATION 20,000 mg/L

Initial NH_3-N (ppm)	Time (min)	pH	ISE Reading (mV)	Corresponding ppm	x (Dilution Factor)	Ammonia removal (%)
600	**Applied Potential = 7.0 V**					
	0	6.54	25.0	60.00	600.00	0.00
	5	3.32	26.0	55.75	557.52	7.08
	10	3.04	26.1	55.53	555.32	7.45
	20	2.76	26.2	55.31	553.14	7.81
	30	2.60	27.2	53.17	531.74	11.38
	50	2.41	29.5	48.56	485.62	19.06
	70	2.27	31.0	45.77	457.72	23.71
	90	2.19	33.2	41.97	419.67	30.05
	110	2.11	36.1	37.43	374.30	37.62
	130	2.09	38.0	34.73	347.28	42.12

APPENDIX - D 1 CALIBRATION CURVE FOR AMMONIA ION-SELECTIVE ELECTRODE (ISE) - FOURTH SET OF EXPERIMENTS (HIGHER NaCl CONCENTRATION)



NH_3-N Concentration (ppm)	Electrode Potential (mV)
0.1	190
1.0	127
4.0	90.5
10.0	67.7
100.0	8.3
1000.0	-49.9

APPENDIX - D 2 AMMONIA REMOVAL FOR VARYING NaCl CONCENTRATION AT A CONSTANT CURRENT OF 3.0 A, UNADJUSTED pH

NaCl concentration (mg/L)	Time (min)	pH	ISE Reading (mV)	Corresponding ppm	x (Dilution Factor)	Ammonia removal (%)
10,000	**Applied Potential = 9.5 V**					
	0	6.22	-14	4.00	40.00	0.00
	5	5.21	-13	3.78	37.78	5.56
	10	4.09	-12	3.60	36.03	9.93
	20	3.51	-7	2.84	28.43	28.92
	30	3.26	-1	2.14	21.40	46.50
	50	3.00	9	1.33	13.33	66.68
	70	3.04	25	0.62	6.25	84.38
	90	3.03	48	0.21	2.10	94.74
	110	3.74	81	0.04	0.44	98.90
	130	4.59	88	0.03	0.32	99.21
20,000	**Applied Potential = 7.4 V**					
	0	6.38	90.5	4.00	40.00	0.00
	5	3.19	92.4	3.94	39.41	1.48
	10	3.11	95.6	3.48	34.84	12.91
	20	3.03	109.5	2.04	20.39	49.02
	30	3.05	192.2	0.08	0.84	97.89
	50	-	-	-	-	-
	70	-	-	-	-	-
	90	-	-	-	-	-
	110	-	-	-	-	-
	130	-	-	-	-	-
30,000	**Applied Potential = 6.8 V**					
	0	6.52	90.3	4.00	40.00	0.00
	5	3.76	95.8	3.46	34.57	13.58
	10	3.37	102.4	2.68	26.81	32.98
	20	3.22	154.2	0.36	3.64	90.89
	30	4.90	199.4	0.06	0.64	98.40
	50	-	-	-	-	-
	70	-	-	-	-	-
	90	-	-	-	-	-
	110	-	-	-	-	-
	130	-	-	-	-	-
50,000	**Applied Potential = 5.5 V**					
	0	6.47	90.5	4.00	40.00	0.00
	5	3.38	95.9	3.44	34.44	13.91
	10	3.24	108.2	2.14	21.44	46.40
	20	4.86	199.4	0.06	0.64	98.40
	30	7.10	211.4	0.04	0.40	98.99
	50	-	-	-	-	-
	70	-	-	-	-	-
	90	-	-	-	-	-
	110	-	-	-	-	-
	130	-	-	-	-	-

APPENDIX - E ION CHROMATOGRAPHY (IC) ANALYSIS RESULTS

SAMPLES WITH INITIAL 400 PPM NH_3-N, 10,000 mg NaCl/L AT 3.0 A CURRENT

Time (min.)	Chloride (mg/L)	NO_3^- - N mg/L	NH_3-N mg/L	Total N mg/L	pH
0	6060.6	0.76	40.00	40.76	6.17
5	7691.0	1.22	32.57	33.78	2.98
10	7673.2	1.39	29.74	31.13	2.96
20	6244.0	2.01	26.84	28.85	2.85
30	6488.0	3.40	24.23	27.63	2.79
50	7084.2	5.23	12.15	17.37	2.66
70	7738.8	7.23	4.98	12.21	2.60
90	6695.9	6.94	3.73	10.67	2.71

SAMPLES WITH INITIAL 100 PPM NH_3-N, 20,000 mg NaCl/L AT 3.0 A CURRENT

Time (min.)	Chloride (mg/L)	NO_3^- - N mg/L	NH_3-N mg/L	Total N mg/L	pH
0	12121.0	2.36	100.00	102.36	5.20
5	10122.8	1.80	91.18	92.99	3.34
10	9217.5	2.85	88.00	90.85	3.14
20	10885.9	5.73	71.12	76.85	2.91
30	10363.9	7.21	64.95	72.15	2.78
50	8896.4	11.77	39.35	51.12	2.63
70	5900.1	12.80	19.12	31.92	2.56
90	7491.0	15.82	6.11	21.93	2.55
110	6915.5	16.58	1.21	17.79	2.87
130	10513.4	20.39	1.02	21.41	3.75

SAMPLES WITH INITIAL 200 PPM NH_3-N, 20,000 mg NaCl/L AT 3.0 A CURRENT

Time (min.)	Chloride (mg/L)	NO_3^- - N mg/L	NH_3-N mg/L	Total N mg/L	pH
0	12121.0	0.00	200.00	200.00	6.20
5	11539.6	0.99	200.00	200.99	3.56
10	10992.9	0.00	174.82	174.82	3.34
20	10010.6	5.73	164.77	170.50	3.03
30	12113.3	6.22	149.89	156.10	2.83
50	9999.9	4.69	121.13	125.82	2.57
70	14069.0	14.08	98.28	112.36	2.50
90	10914.8	18.07	76.95	95.03	2.45
110	13898.9	30.38	56.13	86.50	2.42
130	12806.5	29.77	37.83	67.60	2.41

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Vitae

- Name: Tariq Mohammed
- Nationality: Indian
- Date of Birth: 29.09.1987
- Email: *trqmdk@gmail.com*
- Permanent Address: Bloom, 20/1148, Panniyankara, Calicut, Pin: 673003, Kerala, India

- Master of Science (M.S.) in Civil Engineering (Water Resources and Environmental Engineering), 2015, King Fahd University of Petroleum and Minerals, Dhahran, Kingdom of Saudi Arabia
- Bachelor of Engineering (B.E.) in Civil Engineering, 2009, BSA Crescent Engineering College, affiliated to Anna University, Chennai, India